This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

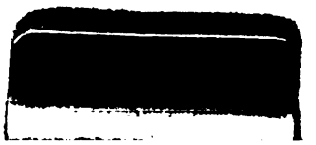
+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

B 454176

CHEM. LIB.
TN
690
.U5
1921a



CHEM. LIBRARY
TN
690
.U5
1921a

DEPARTMENT OF COMMERCE

CIRCULAR

OF THE

U. S. BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 113

STRUCTURE AND RELATED PROPERTIES OF METALS

SEPTEMBER 7, 1921

PRICE, 25 CENTS

Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1921

STRUCTURE AND RELATED PROPERTIES OF METALS [1]

ABSTRACT

The metallographist uses the term "structure" to include those structural features which can be revealed by examination either with the unaided eye or by means of the microscope. By reference to numerous typical metallographic examinations made by the Bureau of Standards the general nature of the structure of metals, the methods for revealing it, and the dependence of the properties of the metal as a whole upon its structural features are discussed.

Macroscopic examination may reveal any or all of the following: Chemical unhomogeneity, crystalline heterogeneity, physical unsoundness, and mechanical nonuniformity. The common methods in use for revealing these features are described and illustrated.

The microscopic examination necessitates the use of a suitable etching reagent. The principles underlying the action of etching reagents are discussed and a list given. The principal conditions which affect structure, chemical composition, application of heat, and mechanical working of the metal are discussed and illustrated by suitable examples. Most important, however, is the effect of structure upon the properties. The dependence of the mechanical properties and chemical behavior upon the structural condition of the material is discussed at considerable length. The results of a large number of "practical applications" of the study of the structure of metals are given to show how an explanation of the "failure in service" of different types of metals and alloys may be reached by this means. Such an explanation can often be arrived at by none of the other testing methods in common use.

CONTENTS

	Page
I. Purpose of circular	4
II. Industrial importance of metallography	6
III. Methods for revealing the structure of metals	8
1. Definition of structure	8
2. Macroscopic examination	8
(*a*) Chemical unhomogeneity and crystalline heterogeneity	9
(*b*) Physical unsoundness	18
(*c*) Mechanical nonuniformity	21
3. Microscopic examination	23
(*a*) Selection of typical specimens	23
(*b*) Preparation of specimens	24
(*c*) Methods of etching	29

[1] Compiled by Henry S. Rawdon, physicist, from results of metallographic examinations made by the Bureau of Standards, except where indicated otherwise.

Page

IV. Conditions affecting structure 33
1. Chemical composition 33
2. Temperature 38
(*a*) Equilibrium changes 38
(*b*) Grain growth 41
(*c*) Phase changes 43
3. Working of metals 46
(*a*) Distortion of crystalline structure 46
V. Effects of structure upon properties 48
1. Mechanical properties 48
(*a*) Hard and soft constituents 48
(*b*) Soft ductile constituents 49
(*c*) Orientation of test specimen with respect to material tested 52
(*d*) Coarsely grained metals 55
(*e*) Physical state of microscopic constituents 57
2. Chemical properties 60
(*a*) Etching 60
(*b*) Solubility of tempered steels 61
(*c*) Corrosion 62
(*d*) Variation in composition throughout an alloy 66
VI. Applications of the microscopy of metals 66
1. Relation to heat treatment 67
2. Supplement to chemical analysis 73
3. Control of metallurgical operations and products 82
4. Construction of constitutional diagrams 88
5. Failure of metals in service 89
6. Service deterioration of alloys 93
7. Miscellaneous 97
VII. Information regarding tests 103
1. Reports 103
2. Tests 103

I. PURPOSE OF CIRCULAR

This circular is not intended to duplicate or to imitate any of the excellent treatises on the subject of metallography which have appeared in print within the last few years. It is desired rather, by reference to a series of typical specimens chosen from a great many which have been submitted to this Bureau for examination, to show the advantages of and the necessity for the metallographic examination as a means of obtaining complete and adequate knowledge of the properties of metallic materials. The circular will also aid very materially in answering the numerous inquiries received by the Bureau concerning proper and suitable methods for revealing metal structures and the interpretation of the results obtained. The circular supplements one of earlier date [2] and, in addition to showing by means of typical illustrations the industrial importance of the method, summarizes different lines of

[2] Metallographic Testing, B. S. Circular No. 42.

metallographic testing for which the Bureau of Standards is equipped. A general view of the laboratory devoted to the study of the structure of metals is shown in Fig. 1.

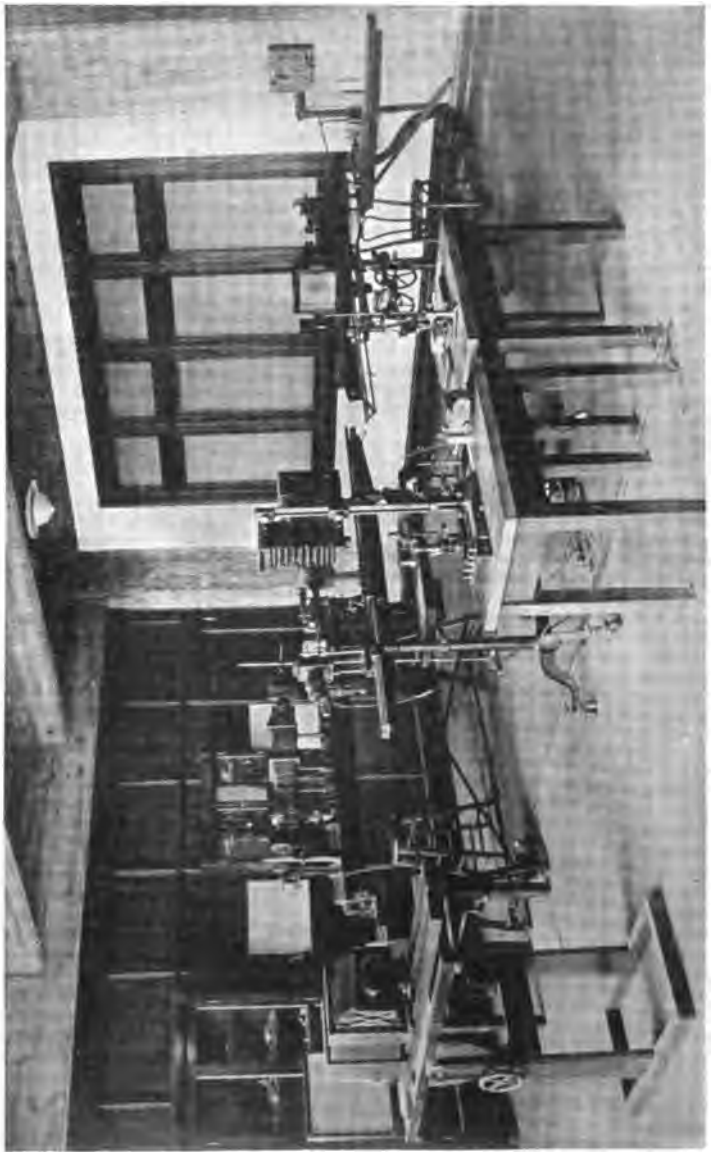


FIG. 1.—*Laboratory for the microscopy of metals at the Bureau of Standards*

The term "metallography" has come to be used by many in a relatively narrow sense as synonymous with "microscopy of metals." As used by the Bureau of Standards, however, the term

includes all those methods of examination which throw some light upon the structure and properties of metals and may properly be considered as synonymous with "physical metallurgy." The study of the structure of metals constitutes, then, only one phase of a complete metallographic examination of any material; subsequent publications similar to this are planned to cover other phases of the subject.

II. INDUSTRIAL IMPORTANCE OF METALLOGRAPHY

It is no longer necessary to offer arguments concerning the importance of the metallographic method. The remarkable growth of metallography in the last few years, together with the proportionately widened scope of its applications, is sufficient and ample evidence of the value of the method. From a relatively unimportant branch of physical chemistry it has been developed into a means of investigation of the properties of metals and alloys on a par with the older methods of chemical and mechanical testing and is very frequently of service in explaining difficulties which are inexplicable by the other and older methods alone.

It is in the metallurgy of iron and steel that the metallographic method has found widest application. This is only a natural consequence of the great industrial importance of steel as well as of the complex nature of the alloy itself. For the purpose of supplementing and interpreting the results of chemical analysis of such metallic products the method is of great importance. By means of preliminary examinations of specimens to be sampled, the unhomogeneity of the material may be determined so that a sample may be chosen in such manner that it will properly represent the material. On the other hand, at times it is desirable to choose the sample so that it will demonstrate in what manner the composition of the special material differs from the normal. Likewise the knowledge gained from the examination will aid in explaining apparent discrepancies obtained in the analysis of samples taken from different parts of the specimen, or from supposedly similar specimens.

The physical properties of an alloy are much more closely related to the minute structure of the material than they are to the ultimate chemical composition. To-day no one questions the value of chemical analysis in metallurgical work, but the metallographic examination when properly interpreted may be of far greater value than the chemical—for example, in explaining the

properties and predicting the uses of the finished product. The nature of the various microconstituents comprising the alloy, their relative size and distribution, the occurrence of extraneous substances or "inclusions," the structural effects of thermal and mechanical treatment, together with other features revealed by the examination, are factors of supreme importance in determining the properties of the material. By way of illustration, a medium carbon steel may be mentioned; this alloy may have mechanical properties ranging at one end from those of a very hard metal of no appreciable ductility and almost impossible to machine, to one at the other extreme, fairly soft and ductile and readily machined. The composition is constant throughout and tells us nothing. For the proper explanation a knowledge of the structural condition which has been brought about by the various treatments to which the metal has been subjected is necessary and usually sufficient.

All tests of metals are for the general purpose of determining the suitability of the material for some specific use; the mechanical properties are therefore in many cases the ultimate criteria. As in the case of chemical analysis the metallographic examination can be made of inestimable service in mechanical testing. The selection of specimens may determine absolutely the validity of any conclusions drawn from tests. Not only may the small test specimens be properly taken so as to represent the larger mass of metal, but the results obtained in the test may be most properly interpreted in terms of the structure of the material, and for purposes of comparison it is necessary that the materials be in the same structural condition. In the following discussion these features are treated more fully.

A knowledge of the chemical composition is essential to a full understanding and interpretation of the structural condition of any metal or alloy, and to a somewhat lesser degree mechanical testing is also. Conversely, a knowledge of the structural condition supplements and explains the results of the other two methods of testing. All three are mutually interdependent and necessary for a full understanding of the properties of any metal.

III. METHODS FOR REVEALING THE STRUCTURE OF METALS

1. DEFINITION OF STRUCTURE

The term "structure" when employed with reference to metals and alloys is used in a somewhat restricted sense. The metal microscopist ordinarily does not include in his definition of this term such characteristics as the minute crystalline structure, the arrangement of atoms, and such other fundamental features of the structure of matter as may be revealed by suitably refined means. The term is used to include those features for revealing which no refinement greater than that of the modern compound microscope is necessary. It should be borne in mind, however, that in a few special cases recourse must be had to very special means for suitably revealing the structural features of the metal.

2. MACROSCOPIC EXAMINATION

The study of the structure of any metal most properly begins with the macroscopic examination of the specimen; that is, with an examination which does not involve any magnification other than that obtained by the use of the simple magnifier. It is quite evident that the knowledge of the gross structure of alloys and metals gained by the preliminary macroscopic examination is very helpful in understanding properly the more minute features revealed by the microscope in exactly the same way that a knowledge of the anatomy of the human body must be used as a background in which to fit the information gained by a study of the histological or minute features of the various tissues which make up the body. Although this survey is usually made for the purpose of revealing chemical unhomogeneity, generally by some suitable etching method, other important structural features are often revealed. Some of these are: Crystalline heterogeneity—for example, relative size, shape, and arrangement of crystal grains, lack of grain refinement, persistence of "casting structure" after heat treatment and mechanical working; physical unsoundness such as "flakes" and internal fractures, blowholes, gas cavities, and porosity; variations in structure due to heat treatment incidental to such processes as welding and oxyacetylene cutting of metals; local deformation caused by such processes as riveting and punching; and other structural features that may occasionally be met. By special methods information relating

to the mechanical state of the metal—that is, the distribution and relative magnitude of internal stresses—may also be gained. The different methods in use for the study of the macrostructure of metals may be best described in connection with the different purposes for which macroscopic examinations are made. In the following discussion the applications for the study of the ferrous alloys will be described in much greater detail than for the non-ferrous ones, inasmuch as the method has been developed for the study of iron and steel to a higher degree than for other metals.

(*a*) CHEMICAL UNHOMOGENEITY AND CRYSTALLINE HETEROGENEITY

One of the most serious and most common of the defects of alloys revealed by macroscopic examination is the lack of chemical homogeneity. Such variations in composition may be brought about in the material intentionally as, for example, in case-hardened steels, partially malleableized cast iron, and similar products, in which case it is hardly to be classed as a defect. In the greater number of examples by far, however, chemical unhomogeneity represents an undesirable state resulting from conditions of manufacture, such as segregation and liquation. Such conditions often are so pronounced that they persist in the metal throughout the different treatments, both mechanical and thermal, that it receives, and so appear in the metal in its finished state. They may thus serve the useful purpose of furnishing a record of the plastic flow of the metal during the various manufacturing operations, as will be referred to later. Variations in the chemical composition of any alloy quite generally result in a differential attack of the material when it is subjected to the action of a corrosive or etching reagent of any kind. The greater the differences in composition in different portions of the metal, the more pronounced are the relative differences in the etch pattern which results.

The most commonly used etching reagent for steels for macroscopic examinations is an aqueous solution of copper-ammonium chloride (Heyn's reagent). The solution usually recommended is approximately 8 per cent in strength, 10 g in 120 cm^3 of water. The solution keeps indefinitely and, if desired, may be diluted somewhat when used. The experience of the Bureau of Standards indicates that a somewhat weaker solution than the above, the specimen being etched two or three times in a fresh solution, if necessary, is the most convenient way to use this reagent. The specimen, after it has been sectioned and roughly polished,

carefully cleaned free from oil marks or finger prints by washing in alcohol or gasoline and then dried, is immersed in the solution, polished surface up. Care must be taken so that the solution quickly covers the entire surface, that no air bubbles are entrapped, and that the liquid is agitated gently; otherwise queer, misleading markings on the etched surface may result. If desired the surface of the metal may be rubbed with a little emery flour on the tip of the finger, washed with water, and immersed while still wet so as to promote the even flow of the etching reagent over it. A coating of spongy copper forms over the face of the specimen; this is easily removed, however, with a swab of wet cotton, if the etching solution was of the proper concentration, and the portions of high carbon, sulphur, and phosphorus content will be found to have been darkened as a result of the etching. If the copper film adheres and can not be removed, because of improper concentration or temperature of the solution, a dilute aqueous solution (approximately 0.5 per cent) of ammonium persulphate will facilitate in its removal.

Results somewhat similar to those of Heyn's reagent may be obtained by the use of a solution of iodine (10 g iodine, 20 g potassium iodide, and 100 cm^3 water). The etch markings are not so clearly defined, however, as in the case of the copper-ammonium chloride solution. The iodine solution was formerly used much more than it is at present.

Concentrated acid may be employed to advantage to reveal chemical unhomogeneity. Hot (100° C) concentrated hydrochloric acid is often used, although others are sometimes preferred by different workers. Such other acids used include 1–1 nitric acid, various concentrations of hydrochloric acid, dilute sulphuric acid (20 cm^3 concentrated acid, 100 cm^3 water), and various other mixtures. The general result is the same in all cases. The highly contaminated portions are etched out, and the surface is roughened considerably. The etch pattern produced by a prolonged attack by a dilute acid is often much less sharp and distinct than one produced in the same material by a rapid attack by a concentrated acid. A prolonged etching—for example, 4 or 5 hours—in 5 per cent alcoholic solution of picric acid is often very useful, however. The deeply etched specimen may be used for producing a permanent record by inking the face with printer's ink and making a print on paper. Fig. 2, which shows the head of a rail submitted to the Bureau of Standards for

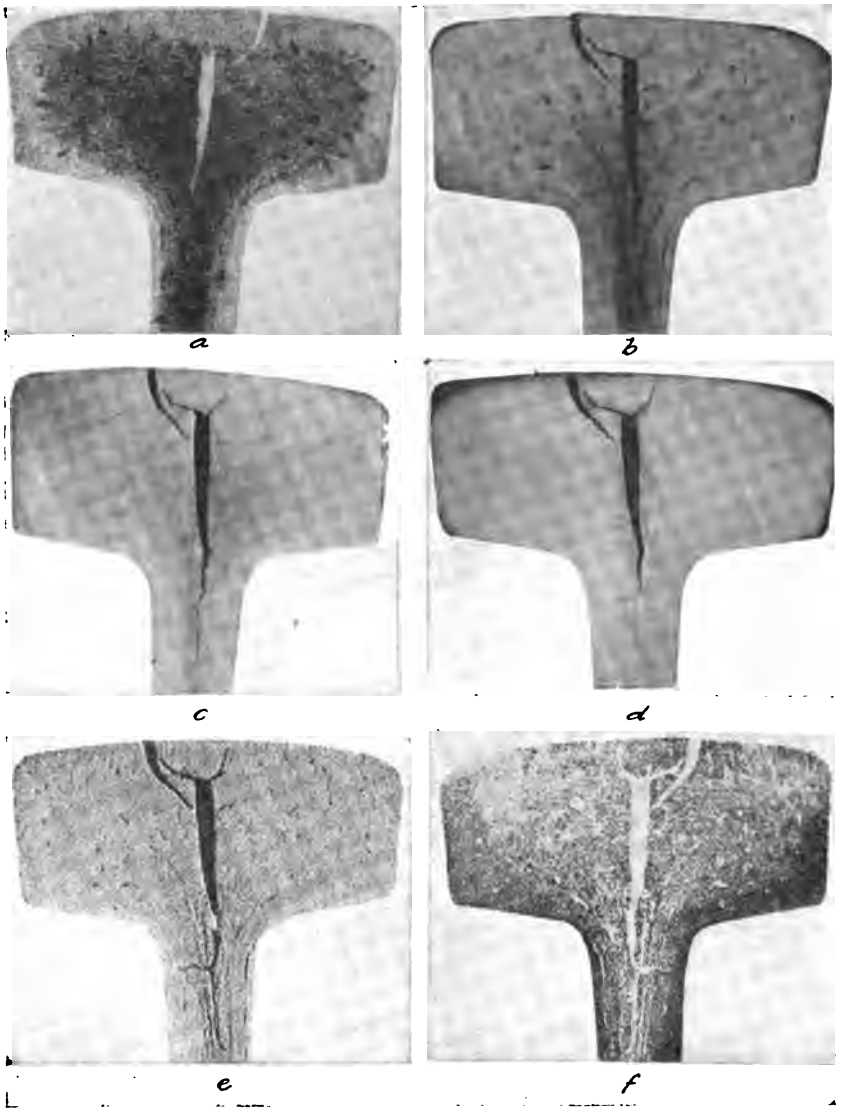


FIG. 2.—*Macrostructure of the head of a segregated rail which failed in service, as revealed by various etching reagents.* × 3/4

Note that some of the reagents are much more effective than others in revealing the segregated center of the head. Although such metal should be regarded with suspicion, it is not to be inferred that segregation of the character shown will of necessity lead to failure of the rail. The character of the service is the decisive factor. Methods of etching: (*a*) Sulphur print, (*b*) aqueous solution of copper ammonium chloride (Heyn's reagent), (*c*) aqueous solution of iodine and potassium iodide, (*d*) acidulated alcoholic solution of cupric chloride (Stead's reagent), (*e*) hot concentrated hydrochloric acid, (*f*) print of the deeply etched surface of *e*

examination after failure in service in the track, illustrates the use of the various reagents described above. It is very evident that the results of chemical analyses of the rail shown by several analysts might differ very materially according to the location in the rail of the sample used for the analysis.

Fig. 3 shows the appearance of a specimen deeply etched with concentrated hydrochloric acid. The specimen was a portion of a large steel casting which broke during shipment. Although the

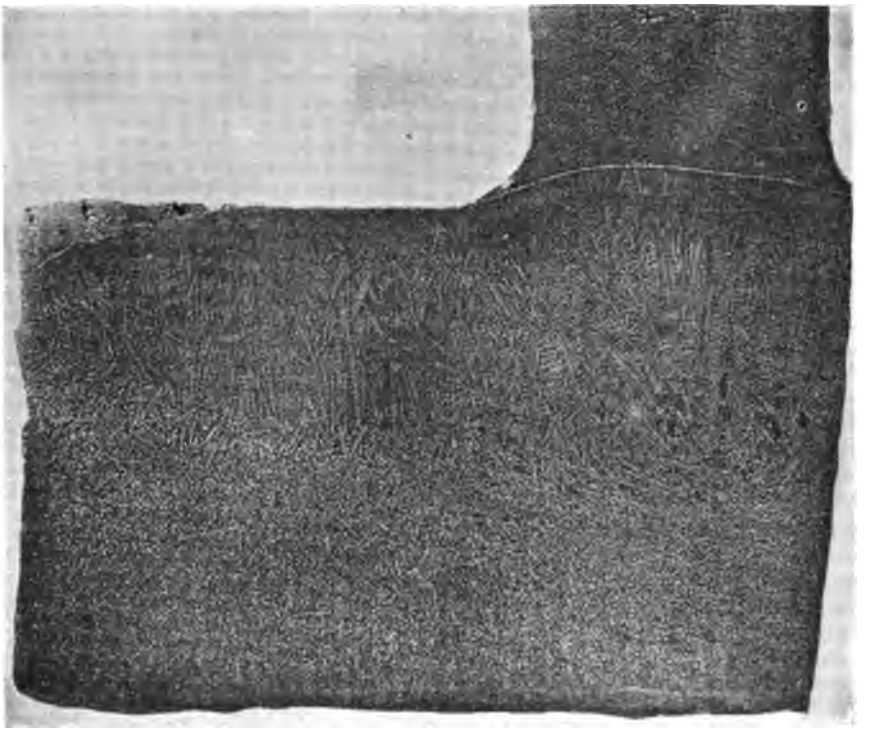


FIG. 3.—*Macrostructure of a defective steel casting revealed by deeply etching with hot concentrated hydrochloric acid.* × 1/2

Note the fern-like pattern which, in steel, is indicative of inferior material

material had been given the usual specified annealing for grain refinement, the metal was so porous and segregated in character that the original structural pattern, and also the accompanying inferior mechanical properties, were largely retained and not materially improved by the annealing.

A reagent of decided merit for revealing the macroscopic features of iron and steel is an aqueous solution of ammonium persulphate (1 or 2 g in 10 cm^3 water). This has long been recognized

as one of the best reagents for etching copper alloys, but its application to the ferrous alloys has been neglected.[3] It reveals

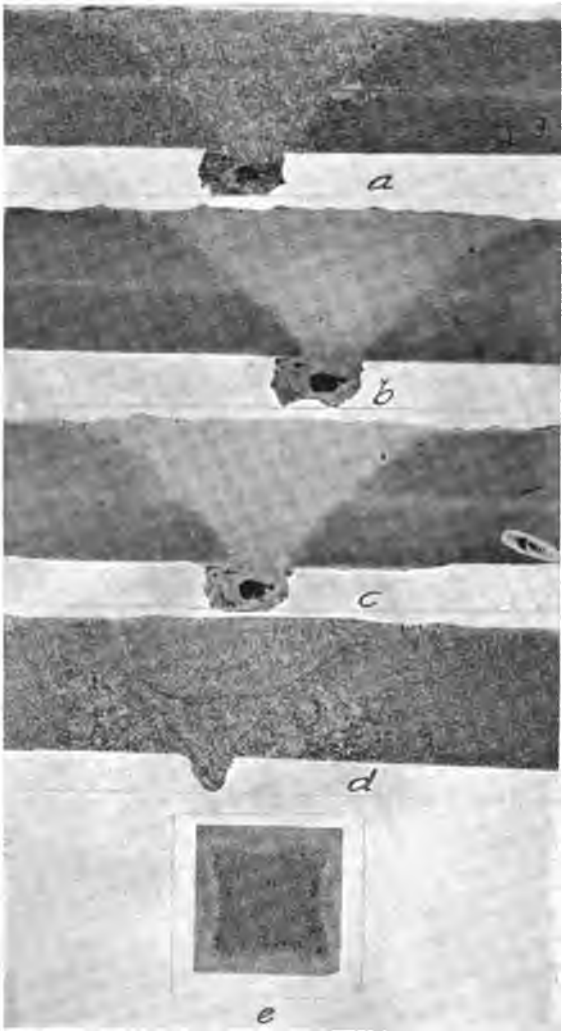


FIG. 4.—*Macrostructure of fusion welds and of segregated steel, illustrating the advantages of ammonium persulphate as an etching reagent.* × 1

A coarsely crystalline condition is usually considered very undesirable in metals. Note that this condition is revealed most plainly by ammonium persulphate. (*a*) Specimen of oxyacetylene welded steel plate etched with aqueous solution of ammonium persulphate; (*b*) specimen *a* etched with aqueous solution of copper ammonium chloride; (*c*) specimen *a* etched with 2 per cent alcoholic nitric acid; (*d*) welded steel plate, similar to *a*, illustrating overheating of the plate, etched with ammonium persulphate; (*e*) cross section of bar of segregated steel, etched with ammonium persulphate

chemical unhomogeneity as well as do the reagents mentioned above and has the added advantage in that it shows crystalline

[3] Henry S. Rawdon, The Use of Ammonium Persulphate for Revealing the Macrostructure of Iron and Steel, B. S. Sci. Papers, No. 402.

heterogeneity in a very striking manner. It is probably the best reagent for iron and steel for showing this phase of the structure. Fig. 4 illustrates results obtained by its use.

In addition to the above reagents a number of others are used, some of which are intended for special purposes. A reagent described for demonstrating the distribution of sulphur and phosphorus in steel is an acidified aqueous solution of mercuric chloride (10 g mercuric chloride; 20 cm^3 hydrochloric acid, 1.12 specific gravity; water 100 cm^3). When the specimen is immersed a black precipitate forms on the areas of high sulphur content, while yellow specks indicate the higher phosphorus areas. The reagent is usually applied on thin silk, which is pressed firmly against the face of the specimen and a permanent print is thus made. The reagent is but little used in this country because the same information may be obtained more easily with other reagents.

The distribution of sulphur is usually shown by the so-called sulphur-print method. The steel specimen is sectioned, and the surface, after being smoothed off with a file, is pressed firmly against a sheet of photographic paper which has been moistened with a dilute sulphuric acid solution. Two cm^3 concentrated acid in 100 cm^3 water is the concentration generally used, though in many cases a more dilute one may be used to advantage. Particularly is this the case with metal very high in sulphur and also for very large specimens where considerable time is needed for placing the paper in position. Mat-finish paper should be used. It is extremely difficult to prevent glossy paper from slipping on the metal surface, in which case a blurred print results. A fine polish of the surface, such as is essential for microscopic examination, is not necessary nor desirable for sulphur printing. Very clear prints can be made on surfaces finished with a medium fine file. Bromide paper or any of the common developing photographic papers may be used. The work of LeChatelier and Bogitch [4] indicates that the darkening of the sensitized surface of the photographic paper is caused by the action of the acid upon the sulphur alone and not by the combined action of sulphur and phosphorus, as has formerly generally been supposed. The assumption is always made, however, that any unhomogeneity which may exist for the metalloids other than sulphur occurs under the same conditions as does that of sulphur, and that the distribution of sulphur

[4] H. LeChatelier and B. Bogitch, "Macrographie des aciers," Rev. de Métallurgie, Memoirs 16, p. 129; 1919.

recorded in the sulphur print is an index of the distribution of the other constituents of the steel also. Fig. 2 shows this similarity of sulphur print to the etch patterns obtained by the usual etching methods. The length of time required for printing depends upon the strength of the acid solution used and the sulphur content of the metal. When steels high in sulphur are used, several prints may be made without regrinding the surface, by progressively increasing the printing time considerably for prints after the first one. By the use of a suitable press, prints which are as clear and definite as the photographs of the etched surfaces may be obtained.

By means of a specially prepared gelatinous emulsion of silver bromide the sulphur-print method may be extended to the study of fractures. Directions for the preparation of the emulsion have been published.[5,6] This special application of the method is but little used, however.

An acidulated alcoholic solution of copper chloride is often used to reveal the distribution of phosphorus. Various formulas for preparing this reagent have been recommended by different investigators. In general, however, the results obtained are very similar for all of them. The formula of Stead (copper chloride, 10 g; magnesium chloride, 40 g; concentrated hydrochloric acid, 20 cm^3; and alcohol to make 1000 cm^3) and that of LeChatelier (95 per cent alcohol, 100 cm^3; water, 10 cm^3; copper chloride, 1 g; picric acid, 0.5 g; and concentrated hydrochloric acid, from 1 to 3 cm^3) may be cited as representative. After an immersion of about one minute, the previously polished and cleaned surface of the specimen will usually be found to be covered in certain portions with a firmly adhering film of copper. Other parts remain clear or uncoated. The copper-coated portions are generally considered to be of lower phosphorus content than the clear or slightly coated portions. Other elements in solid solution, however, such as nickel, may produce a similar differential precipitation of the copper, and the work of LeChatelier and Bogitch [7] appears to indicate that the reagent is primarily useful for demonstrating the distribution of oxide within the steel, the other indications being only secondary ones. Fig. 5 shows a portion of a shrapnel shell which was etched with this reagent.

---

[5] F. Rogers, "The investigation of fractures," J. Iron and Steel Inst., 85, p. 379; 1912.

[6] A. Portevin, "Les cassures défectueuses," Rev. de Métallurgie, Memoirs, 16, p. 340; 1919.

[7] H. LeChatelier and B. Bogitch, "Macrographie des aciers," Rev. de Métallurgie, Memoirs, 16, p. 129; 1919.

The cupric reagents have largely supplanted the method of heat tinting for showing the distribution of phosphorus. However, this latter method is very useful for cast iron, particularly for microscopic examination, as will be referred to later.

For revealing the macrostructural features of brasses, bronzes, and similar alloys of high copper content, an aqueous solution of ammonium persulphate is very often employed, although an acidified solution of ferric chloride or an ammoniacal solution of copper-ammonium chloride may be used with very good results. The relative size and arrangement of the crystals are the features in which one is most interested; that is, in addition to the matter of soundness in the case of castings. In this case, however, an

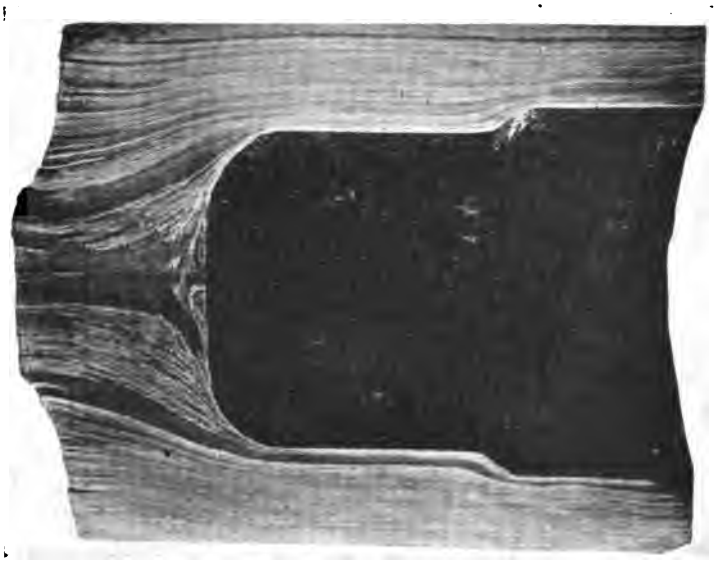


FIG. 5.—*Macrostructure of forged steel (longitudinal section of the head of a shrapnel shell) revealed by etching with cupric chloride (Stead's reagent).* × 4/5

The "banded" structure indicates a nonuniform distribution of phosphorus in the steel and is conducive to brittleness particularly when the material is stressed transversely to such streaks

etching is usually unnecessary. In Fig. 6 specimens are shown to illustrate the usual macroscopic features of copper alloys.

The reagent commonly employed for etching aluminum and its alloys to reveal the macrostructure is an aqueous solution of sodium hydroxide (approximately 10 per cent). It is customary to heat the specimen in the solution until the surface is sufficiently etched. A combination of alkali and hydrofluoric acid etching has been highly recommended by Carpenter.[8] The specimen is

[8] H. C. H. Carpenter and C. F. Elam, "Crystal growth and recrystallization in metals," J. Inst. of Metals. 4; 1920.

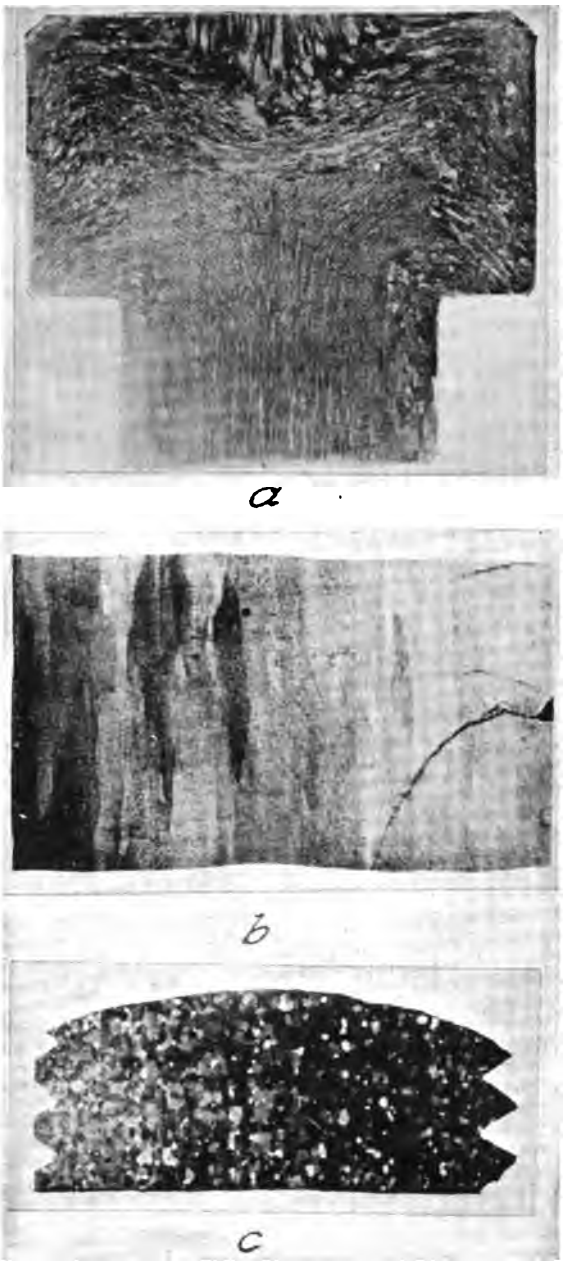


FIG. 6.—*Macrostructure of a forged copper alloy, manganese bronze, revealed by etching with an ammoniacal solution of copper ammonium chloride*

Note the cracks which occurred in service in the coarsely crystalline specimens, *a* and *b*; presumably this was largely the result of the crystalline condition of the material. (*a*) Longitudinal section of the head of a forged bolt which cracked in service (× 1½); (*b*) longitudinal section of bolt which failed in service (× 3); (*c*) longitudinal section of bolt (× 2)

51646°—21——2

etched in an alcoholic solution of sodium hydroxide to remove the "flowed" surface metal. When the surface has been faintly etched, the sample is transferred to a dilute aqueous hydrofluoric acid solution (1 or 2 per cent) and allowed to remain until the etching is complete.

Fig. 7 shows specimens of an aluminum alloy, designated as "conducting aluminum" and of the approximate composition—silicon, 0.5 per cent; iron, 0.5 per cent; magnesium, 0.7 per cent; aluminum, remainder—etched so as to reveal the macrostructure.

The occurrence of minute pores of intercrystalline cavities in castings of light aluminum alloys is a matter of grave importance. Their presence can often be detected in suspected metal by immersing a polished specimen in alcohol colored with picric acid or some other brightly colored dye. The specimen, after rapid washing to remove all traces of the dye on the surface, is dried and allowed to stand in a warm place. The porosity of the metal is often indicated by the appearance of colored spots on the surface as the colored alcohol evaporates from within the internal cavities in which it was inclosed.

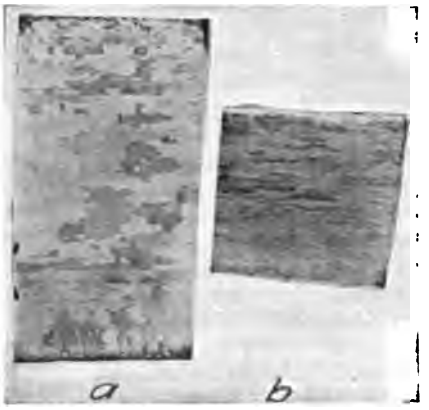


FIG. 7.—*Macrostructure of a wrought aluminum alloy.* × 2

Etching reagent, 10 per cent aqueous solution of sodium hydroxide

(*b*) PHYSICAL UNSOUNDNESS

Much of the evidence of this phase of the structure of metals is furnished by a simple visual examination. In case the unsoundness is of a minute character the method described above for aluminum may be used. In other cases very special means must be used. If the surface of the specimen is carefully machined, a very light finishing cut with a very sharp tool being made, evidence as to the true state of the soundness of material is often made available which can be obtained in almost no other way. The ordinary methods which involve polishing and etching exaggerate the features of unsoundness to a considerable degree. In many alloys and metals which are rather coarsely crystalline careful machining is often sufficient also to reveal the structure of the material to a very surprising degree.

An examination by means of X rays is often of value if the specimen is not too large. The features revealed by this method of examination are primarily those which result from considerable differences in density, hence it is of great value in locating internal cavities and similar flaws. Ordinary segregation can not be revealed by this means, although it has been successfully used in detecting such features of composition as resulted from the addition of a lead alloy for filling cavities in light aluminum castings. Specimens of steel to be examined by this means should not exceed one-half inch in thickness. As a general rule, the thicker the specimen the more pronounced must be the defect in order that its presence can be revealed by this means. This Bureau has found radiographic examination most useful in following the effect of a series of successive treatments, thermal and mechanical, upon certain internal defects such as are shown in Fig. 8. The flaws revealed by the radiographic examination are of the same character as those described later (Sec. V, 1, *c*). It is evident from Fig. 8 that they have not been eliminated by the treatments to which the steel was subjected. On the other hand, they appeared to have been accentuated. This method has also been used to advantage in the examination of test bars preliminary to carrying out a test, particularly such tests as are very time consuming, as fatigue, or such tests as would be influenced greatly in their results by internal defects, for example, impact.[9]

For detection of cracks, such as may be produced by hardening by quenching and similar operations upon steel, a magnetic method will be found very useful. The method is particularly valuable for revealing them in an early stage in the shaping of an article—for example, precision gages and similar pieces which must be ground to size—so that defective specimens may be discarded without much expenditure of wasted effort. The roughly polished specimen is magnetized and then immersed in a light oil containing very fine iron dust in suspension. Kerosene and "cast-iron mud," such as is obtained from lapping disks, may be used. The iron particles bridge across any slight discontinuity in the surface of the specimen and locate very accurately the system of surface cracks. The excess of iron dust may be removed by bathing the specimen in alcohol or clean kerosene. The method has also been successfully used for the detection of

[9] Henry S. Rawdon, "Some applications of metal radiography," Proc. Am. Iron and Steel Inst.; October, 1919.

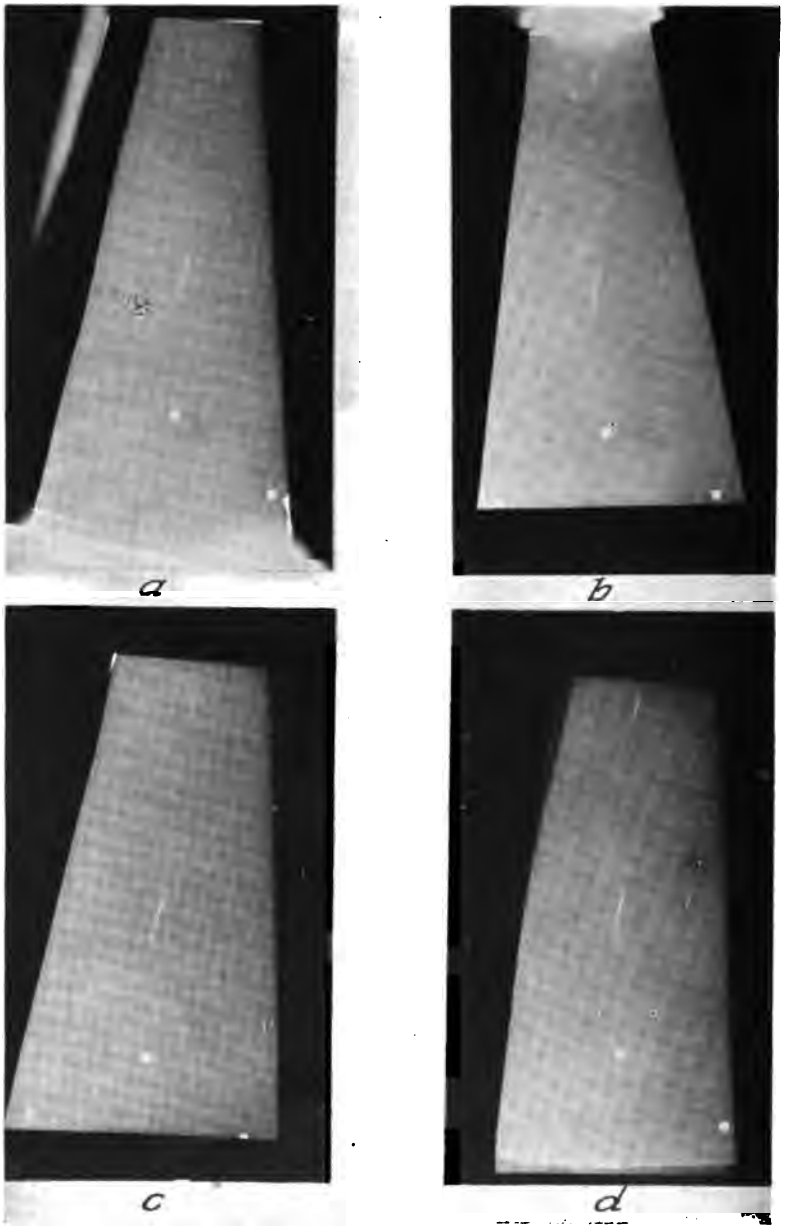


FIG. 8.—*Defects, "flakes," in forged gun steel revealed by radiographic examination. Approximately* × 1

A radiograph of the specimen was taken after each of the treatments listed below. The steel plate ¼ inch thick, containing three holes (white spots in radiographs) drilled partly through for reference points, was placed so that the direction of the X-rays coincided with the plane of the defect. Each white line in the radiograph represents a "flake" or defect. Treatments: (*a*) Forging, as received, (*b*) specimen *a* after annealing 30 minutes at 900° C. furnace cooled, (*c*) specimen *b* heated 30 minutes at 900° C and quenched in oil, (*d*) specimen *c* heated 30 minutes at 1050° C and quenched in oil. The successive radiographs indicate the persistence of the defects after the thermal treatments given the material. Exposure, 9-inch spark, 2 milliamperes, 7 minutes

internal fractures in wrought-steel parts.[10] Fig. 9 shows specimens which have been treated in this manner.

(*c*) MECHANICAL NONUNIFORMITY

The examination of metals for mechanical nonuniformity—that is, for the presence of internal stresses of high magnitude which may later lead to serious deterioration—may be noted here.

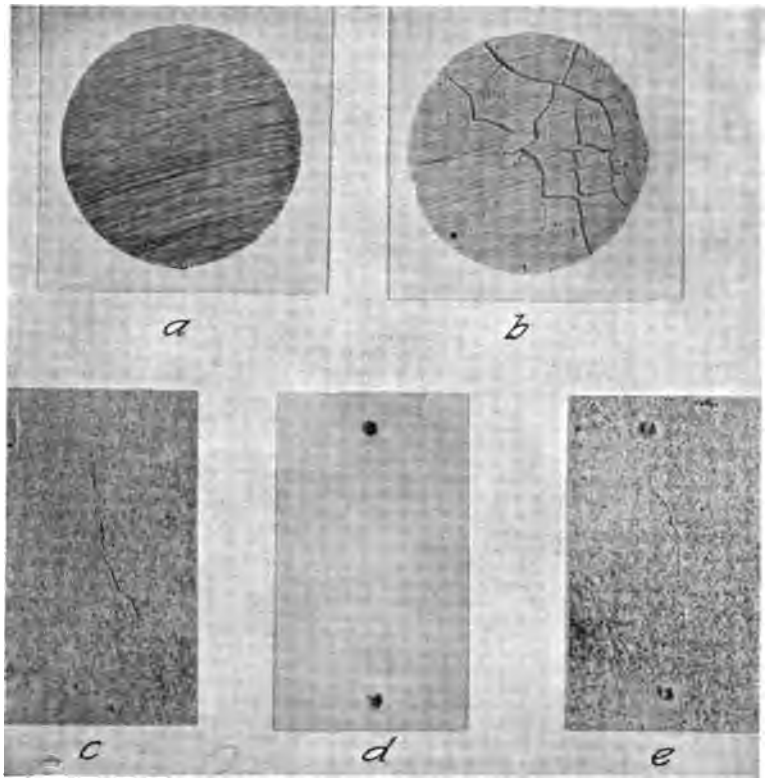


FIG. 9.—*Physical unsoundness of steel revealed by magnetic examination*

(*a*) Roughly polished surface of a precision gage block. × 1½. (*b*) Same as *a*, magnetized and bathed in kerosene containing fine iron dust in suspension; note the network of fine "hardening" cracks revealed. × 1½. (*c*) Section of steel from head of a rail containing internal fracures revealed by method of *b*. × 3. (*d*) Same specimen as *c* after locating the defect by a punch mark at each end. After removing the iron dust no trace of the discontinuity could be seen. × 3. (*e*) Same specimen as *d*, retreated as given in *b*. × 3

Fig. 10 *a* shows a portion of a cold-worked rod of manganese bronze which has been immersed in a solution of mercurous nitrate acidulated with nitric acid. The cracks which were formed by the action of this reagent may be taken as an indication of what would undoubtedly have occurred spontaneously later in service.[11]

[10] H. S. Rawdon and S. Epstein, Metallographic Features Revealed by the Deep Etching of Steel, B. S. Tech. Papers, No. 156.

[11] H. S. Rawdon, "The use of mercury solutions for predicting the season cracking of brass," Proc. Am. Soc. for Testing Materials, 17, part 2, p. 189; 1917.

Materials which crack readily when treated in this manner can be shown by other means to be highly stressed internally.[12]

Steel parts such as balls and roller bearings which are very vigorously hardened indicate by their behavior upon etching in the proper manner that a similar condition obtains there. Fig. 10 *b* shows several hardened steel balls which split when they were etched with hot concentrated acid; cold-rolled steel shafting will sometimes behave similarly when etched in the same manner.

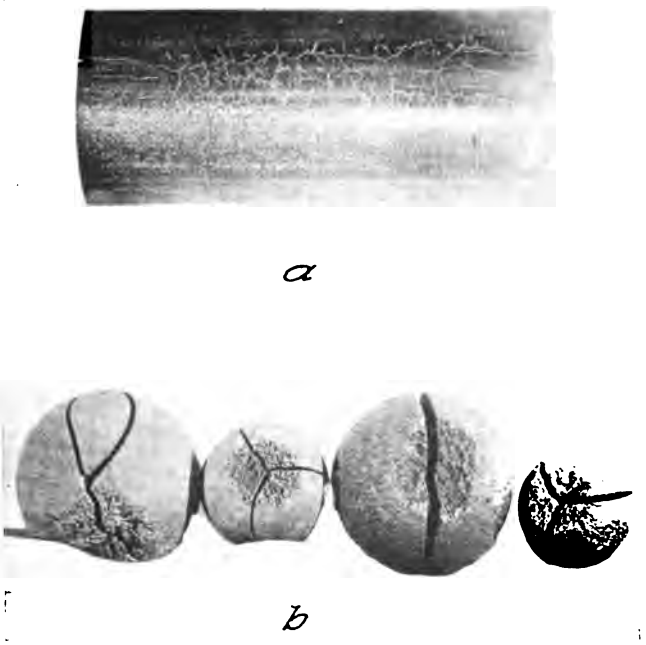


FIG. 10.—*Mechanical nonuniformity of wrought metals revealed by deep etching*

Cracks resembling those shown resulting from deep etching may be produced "spontaneously" in service in metals highly stressed internally. (*a*) Section of a 1-inch manganese bronze rod etched with an acidulated aqueous solution of mercurous nitrate (65 g mercurous nitrate, 15 cm^3 nitric acid per liter). × 1. (*b*) Hardened steel balls which split open when deeply etched with concentrated hydrochloric acid. × 2

The cracking of the metals illustrated above when subjected to the proper etching reagents, and the similar deterioration, "season cracking," which may occur spontaneously in service, are not to be regarded simply as a result of structural variations. However, the distortion of the structure in the cold-worked metals in which such conditions occur is very pronounced and undoubtedly is

[12] P. D. Merica and R. W. Woodward, Failure of Brass: 1.—Microstructure and Initial Stresses in Wrought Brasses of the Type 60 Per Cent Copper and 40 Per Cent Zinc, B. S. Tech. Papers, No. 82.

contributory in a very large degree to the unusual behavior of the metal.

The various features revealed by the microscopic examination of metals may be summarized under the following types:

1. Chemical unhomogeneity, the result of segregation, liquation, decarburization, cementation, and similar causes. In wrought metals lack of complete chemical homogeneity often serves the useful purpose of furnishing a record of the plastic flow of the metal during the various manufacturing operations. This is generally revealed by etching.

2. Crystalline heterogeneity, resulting from the rate of cooling and local variations in the cooling. Local overheating may also contribute to this. Etching with ammonium persulphate is admirable for revealing crystalline heterogeneity in both steel and copper alloys.

3. Mechanical nonuniformity, or presence of internal stresses. When the condition is very severe it may be revealed by deep etching with mercury solutions for copper alloys and concentrated acids for steels.

4. Physical unsoundness, blowholes, porosity, "flakes," internal discontinuities, etc. X-ray and the magnetic examination, in addition to visual examination, may be used to show such features.

3. MICROSCOPIC EXAMINATION

(a) SELECTION OF TYPICAL SPECIMENS

The purpose of the microscopic examination will usually be the deciding factor in the selection of the specimens. However, there are certain principles which may be mentioned governing the sampling of materials for examinations of this kind. Areas of segregation (as determined by a preliminary macroscopic examination) must be carefully avoided if a structure representative of the alloy is desired for observation; on the other hand, specimens should be taken from the zone of segregation if the subject of impurities is of prime consideration. Usually, for alloys which have been mechanically worked, specimens should be chosen so as to represent the changes brought about by the working; that is, sections parallel to and others perpendicular to the direction of working should be examined. In materials which proved defective in service, some specimens at least should be taken immediately adjacent to the fracture, or defects. In such cases as these, in which the metal up to the extreme edge of the

specimen must be examined, the specimen must be protected in some way during the process of grinding and polishing. A method for doing this is described below.

(*b*) PREPARATION OF SPECIMENS

During the preparation—that is, the grinding and polishing—of the specimens for microscopic examination the edges are rounded and beveled off somewhat unless care is taken to protect them. In many cases such a precaution is absolutely necessary, for example, casehardened steels, coated metals, the fractured ends of test bars, etc. Often specimens available are too small for use unless held in some kind of a matrix. For all such cases it is very convenient to coat the specimen with a heavy deposit of electrolytic copper, to mount it in a matrix of some kind, and then to cut and polish a section through the resulting duplex specimen.

The common acid-sulphate bath, consisting of 250 g crystallized copper sulphate, 50 g (approximately 30 cm^3) concentrated sulphuric acid, and water sufficient to make one liter of solution, may be used for the solution in which the specimens are copper-plated. For iron, steel, zinc-coated articles, and the like, it is necessary to plate the specimen with a thin coating first in a slightly alkaline bath before using the acid-sulphate bath, otherwise a spongy deposit will result if the specimen is inserted directly into the acid-sulphate bath. This preliminary coating may be very conveniently deposited by means of a cuprous cyanide bath. Such a solution may be made as follows: The precipitate formed by mixing aqueous solutions of 300 g each of copper sulphate and sodium carbonate (crystallized) is added to 5 liters of water. This is then reduced to the cuprous condition by adding 1 liter of water containing 200 g sodium bisulphite. A more convenient way, however, is to bubble sulphur dioxide gas from a cylinder of the liquefied gas through the liquid and the suspended precipitate until the color indicates that the reduction is complete. One liter of water in which 250 g crystallized sodium carbonate have been dissolved is added, this is followed by a liter of water containing 250 g potassium cyanide in solution, and the whole, which upon shaking should give a clear solution, is diluted to a volume of 10 liters. Cuprous cyanide for the direct preparation of the solution may be purchased from most dealers of electroplaters' supplies.

In many cases, particularly with copper alloys, it is very desirable to deposit a preliminary layer of nickel before the heavy copper layer is added, so that there will be no uncertainty as to the line of demarcation between specimen and coating. This has been found very necessary in such problems as the microscopic study of corrosion of brasses and bronzes. A very convenient solution may be made up as follows: Nickel ammonium sulphate, 90 g; ammonium chloride, 22.5 g; boric acid, 15 g; and sufficient water to produce a volume of 1 liter.

After the specimens are heavily plated they are mounted as follows: A short section of brass or other tubing is filed smooth on one end and placed, with this smoothed end down, upon a block of graphite. The specimen is placed inside the tube with the face to be examined down and then backed up with a matrix. Molten 50–50 lead-tin solder is used a great deal where gentle heating of the specimen is not objectionable. In the case of hardened steels, etc., an alloy of very low melting point, for example, Rose's alloy (lead, 28 per cent; tin, 22 per cent; and bismuth, 50 per cent; melting point, approximately 95° C) or Wood's alloy (lead, 25 per cent, tin, 13 per cent; bismuth, 50 per cent, and cadmium, 12 per cent; melting point 65° C) may be used. A much cheaper substitute that is very suitable for almost all classes of work is made by mixing litharge (PbO) and glycerin in the form of a thick paste. This is poured around the specimen and will set and form a very hard surface which does not interfere with the polishing of the metal. It is sometimes necessary, however, to detach the specimen from such a matrix after polishing before etching; this is particularly true if alkaline reagents such as sodium picrate are used. Often it is very convenient to cut a cavity in the graphite block so that the specimen which is inserted into the depression will project beyond the face of the solidified matrix which holds it. The projecting portion is then cut off with a fine hack saw and the metal ground and polished without removing as much of the whole as would have been necessary if the specimen had been mounted flat within the ring.

In Fig. 11 some applications of the plating and mounting of metallographic specimens are shown.

The subject of the mechanical preparation of metal surfaces for microscopic observation has been discussed in detail in all of the reference works on the subject of metallography and need not be repeated here. The precaution that should be always borne in

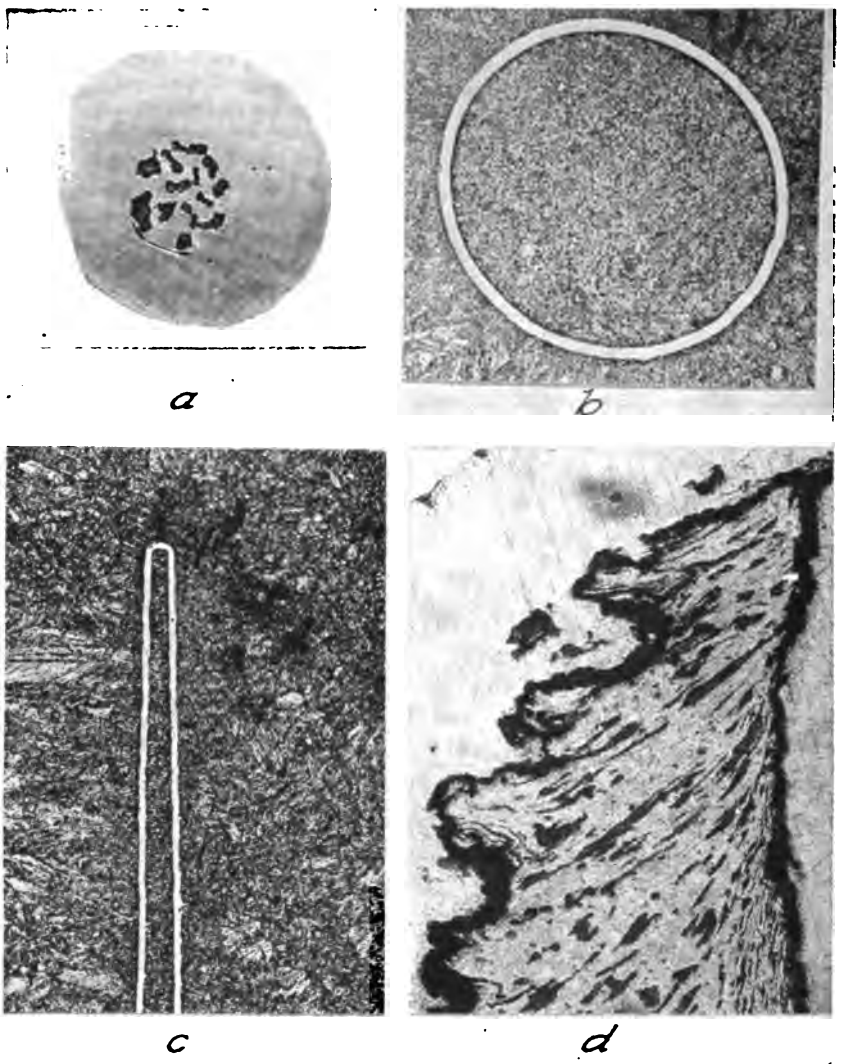


FIG. 11.—*Illustrations of the proper method of mounting very small metallic specimens for microscopic examination*

(*a*) Polished face of a specimen prepared for microscopic examination. The material to be examined, copper wire 0.015 inch diameter, was electrolytically plated with nickel and with copper, embedded in a matrix of molten tin-lead alloy (solder), and a section of the duplex specimen, after cooling, was prepared. × 1. (*b*) Cross section of one of the small wires of *a*. The white ring is the layer of nickel, outside of this a heavy layer of electrolytic copper was deposited. × 100. (*c*) A wire similar to that of *b* was rolled to a strip 0.003 inch in thickness before mounting in the manner described. × 100. (*d*) Small fragment of a lathe-turning of mild steel electroplated with copper and mounted. × 100. Etching reagents: *b* and *c*, Ammoniacal solution of copper ammonium chloride; *d*, 5 per cent alcoholic solution of picric acid

mind as a guide in this work is that a buffed surface is not suitable. A cutting action must be maintained throughout. The number of steps varies considerably with different alloys and with different workers. The following method has been found very suitable at this Bureau for the preparation of ordinary specimens—steels, brasses, etc.

Grinding motors with a variable speed of 500 to 1,200 rpm which carry aluminum disks at each end of the armature shaft are used. To these disks emery paper is attached; the number of grades of paper used varies, for the greater part of the work three steps having been found sufficient after the preliminary smoothing of the specimen with a file, surface grinder, emery wheel, etc. These are domestic (American) emery paper ½, Hubert (French) 1 G, and Hubert 0 or 00. It is very essential that the specimen have a flat surface at the start, otherwise the process of polishing is very long, tedious, and expensive in time and supplies.

The grinding of the specimen with the finest emery paper is followed by wet grinding on cloth-covered disks, kersey being used in preference to the usually recommended broadcloth. As a fine abrasive "3 F alundum" and "S F emery flour" are very suitable. The final polishing is done on a similar cloth-covered disk by means of levigated alumina.

The lack of a uniform method among manufacturers for designating the different grades of emery papers, emery powders, etc., renders it difficult to describe concisely the preparation of the surface. For this reason there is shown in Fig. 12 the surface condition resulting from the use of various grades of papers and abrasive powders upon a specimen of annealed medium-carbon steel.

The procedure given above must often be changed to suit the alloy; for example, aluminum is best prepared by cutting on a fine file under kerosene, grinding at low speed on the finer grades of emery paper which are kept wet with alcohol, kerosene, or the like, and then finished by hand on a cloth-covered polishing block with fine levigated alumina. Other soft alloys and metals can be prepared similarly.

For the examination of some unusual features of structure it is sometimes desirable to carry out the entire process by hand. These cases, however, are quite rare. It has recently been shown [18] that the working of the surface during the process of grinding

[18] H. C. H. Carpenter and C. F. Elam, Crystal growth and Recrystallization in metals, J. Inst. of Metals, No. 2; 1920.

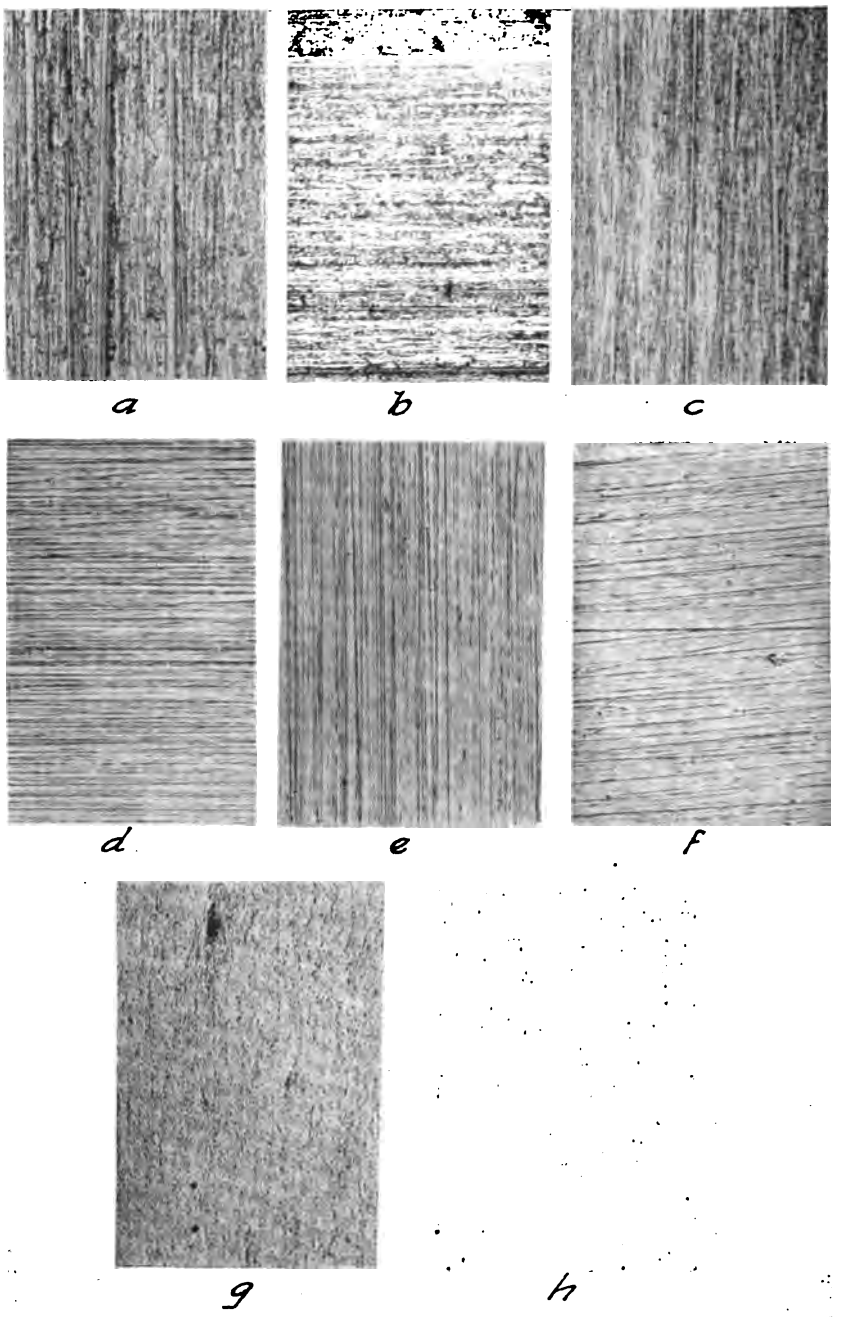


FIG. 12.—*Appearance of the face of a specimen of mild steel in different stages of preparation for microscopic examination.* × 100

Abrasive materials used: (*a*) American emery paper, manufacturer's number, ½; (*b*) American emery paper, manufacturer's number, oo; (*c*) French (Hubert) emery paper, manufacturer's number, 1G; (*d*) Emery paper similar to *c*, manufacturer's number, o; (*e*) Emery paper similar to *c*, manufacturer's number, oo; (*f*) "Alundum" powder, manufacturer's number, 3F; (*g*) Emery flour, manufacturer's number, SF; (*h*) "Levigated" alumina. In stages *a* to *e*, inclusive, the specimen was polished dry; stages *f*, *g*, and *h* were carried out on kersey-covered discs which were kept moist

and polishing is sufficient to cause recrystallization of the surface metal in the case of some of the softer metals and alloys. The real structural condition of the metal can be revealed only by a series of alternate polishings and etchings; the supplementary etching during the process of preparation is for the purpose of removing the recrystallized metal at the surface.

(c) METHODS OF ETCHING

For the microscopic examination of most alloys the polished surface of the specimen must be properly etched in order to reveal the structure, although a preliminary examination of the polished but unetched material should be made because some features, for example, inclosures, are best seen and recognized when the specimen is unetched or at least only slightly etched. While there are certain general principles which must be observed in the choice of a suitable etching reagent for any particular alloy, there is without doubt more chance here for individual preference than in any other phase of the study of metal structures. A comprehensive study of the action of the various metallographic etching reagents upon different types of metals and alloys is in progress at this Bureau.

The results already obtained [14] indicate that oxidation is of fundamental importance in the successful etching of copper and the copper-rich alloy and presumably also for a great many of the other alloys. Many reagents which ordinarily have only a very slight solvent action upon copper or copper alloys may be used successfully for purposes of etching if the action is intensified by oxidation. This may be done either by additions of oxidizing reagents or by passing oxygen gas through the etching reagent while the specimen is immersed.

In some cases the use of two or more different types of etching in succession for the same specimen is desirable, no attempt being made to remove the results of the first etching before the second reagent is used. The second or supplementary etching may be either for the purpose of making prominent a constituent or structural condition not plainly revealed by the first reagent (Fig. 18 *a* and *b*), or for removing a surface film caused by the products of first-etching reaction. This is often necessary in etching with silver nitrate, as an obscuring film of silver precipitated over the face of the specimen must be removed before the

[14] H. S. Rawdon and M. G. Lorentz, Metallographic Etching Reagents: I, for Copper, B. S. Sci. Papers, No. 399.

true structure of the etched metal is revealed. However, this may often be removed with a moist cotton swab. Likewise, in the etching of aluminum an obscuring black deposit resulting from the action of the etching reagent must be removed by immersing the etched specimen in a suitable second solution.

Below is given a list of most of the common reagents in use at the Bureau of Standards. To give anything like a complete list or instructions for use is manifestly impossible.

TABLE 1.—Metallographic Etching Reagents for Revealing Microstructure

Material	Method of etching	Remarks
Copper and copper-rich alloys (brass, bronze, aluminum bronze)	An ammoniacal or an acid oxidizing solution	Suitable oxidizers for use: Hydrogen peroxide, ammonium persulphate, potassium permanganate, potassium dichromate, chromic acid, ferric chloride
	Ammoniacal solution of copper-ammonium chloride	Electrolytic in its nature
	Oxidizing acids	Nitric acid and chromic acid
	Aqueous solution of silver nitrate	The film of precipitated silver must be removed
	Concentrated ammonium hydroxide	Accompanying oxidation is necessary to produce satisfactory results
	Heat tinting	Valuable for certain bronzes
Aluminum and aluminum-rich alloys	Hydrofluoric acid	An approximately 10 per cent aqueous solution is used, a supplementary immersion in concentrated nitric acid or in chromic acid may be necessary to clean the surface
	Aqueous solution of sodium or potassium hydroxide	0.1 per cent aqueous solution is suitable for revealing the constituents, more concentrated sulutions for grain boundaries
Lead	Nitric acid	
Lead and tin alloys, including "white metals"	Dilute nitric acid	Alone or with an addition of chromic acid
	Dilute hydrochloric acid	
	Aqueous solution of silver nitrate	
Nickel	Concentrated nitric acid	Used alone or in a solution of glacial acetic acid, approximately nitric acid 50, acetic acid 40, water 10 per cent
	Electrolytic etching	
	Ferric chloride	
	Dilute sulphuric acid containing an oxidizer (hydrogen peroxide or potassium permanganate)	
	Concentrated hydrochloric acid	A long etching period is required, one hour or so
Nickel-rich alloys (Monel metal, Benedick nickel, nickel brass, invar, etc.)	Same as for nickel	Same as for nickel
	Ferric chloride	
	Ammonium persulphate	
Zinc and zinc-rich alloys	Sodium hydroxide; mixture of chromic and nitric acid; ammonium chloride; iodine; ammonium persulphate	Alcoholic solutions, approximately 1 per cent
	Electrolytic etching	
Gold, platinum, and "noble" metals and alloys	Aqua regia	
Silver and its alloys with copper	Nitric acid; ammonium persulphate solution	
Wrought iron, "pure" iron	Nitric acid	2 per cent alcoholic solution, commonly used
	Picric acid	5 per cent alcoholic solution
	Cupric reagent	To reveal phosphorus banding, and similar structural features

TABLE 1.—Metallographic Etching Reagents for Revealing Microstructure—Contd.

Material	Method of etching	Remarks
Carbon steels	Nitric acid, picric acid, and cupric reagent, as above	
	Hot alkaline sodium picrate or other oxidizers	Used to color cementite
	Hydrochloric acid	1 per cent alcoholic solution
Alloy steels	Same reagents as for carbon steels above	
	2 per cent alcoholic picric acid, very prolonged etching	For revealing grain boundaries
	Sodium picrate and other oxidizers	For steels showing free carbide
Cast iron	Picric acid, or nitric acid as above	
	Heat tinting	To identify iron phosphide and manganese sulphide
	Sodium picrate	

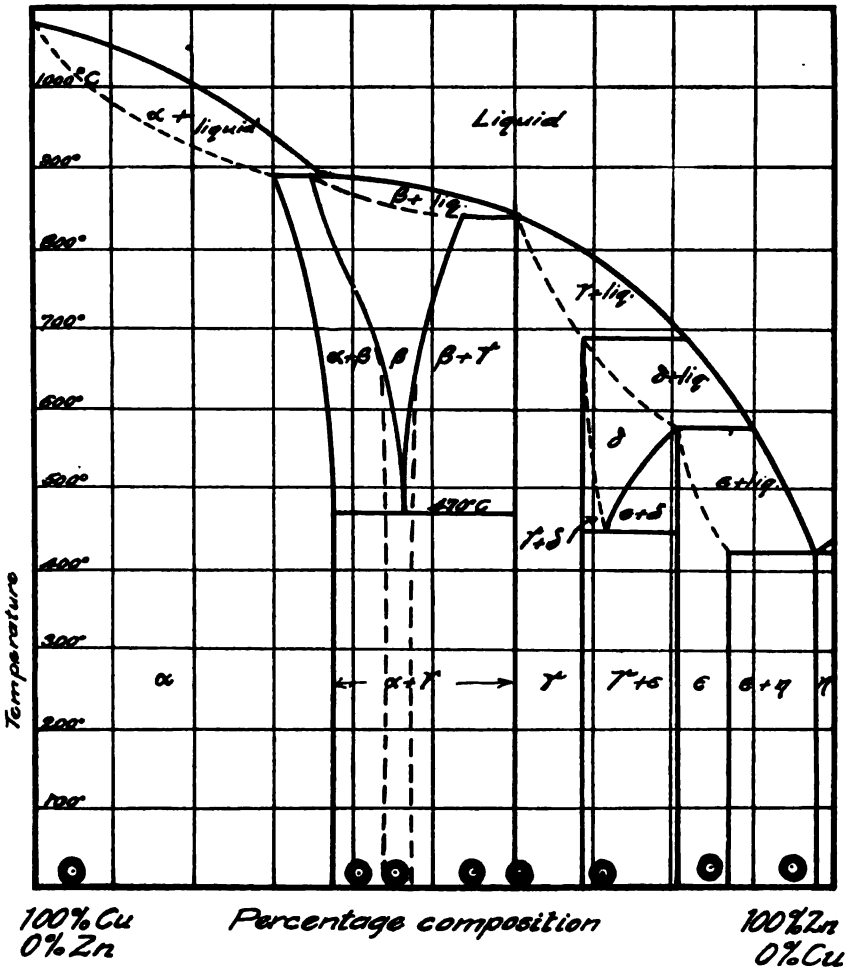


FIG. 13.—*Constitutional diagram of the copper-zinc series of alloys*

The microstructural features of the different types of alloys, the composition of which is indicated by the circles at the base of the diagram, are shown in Fig. 14

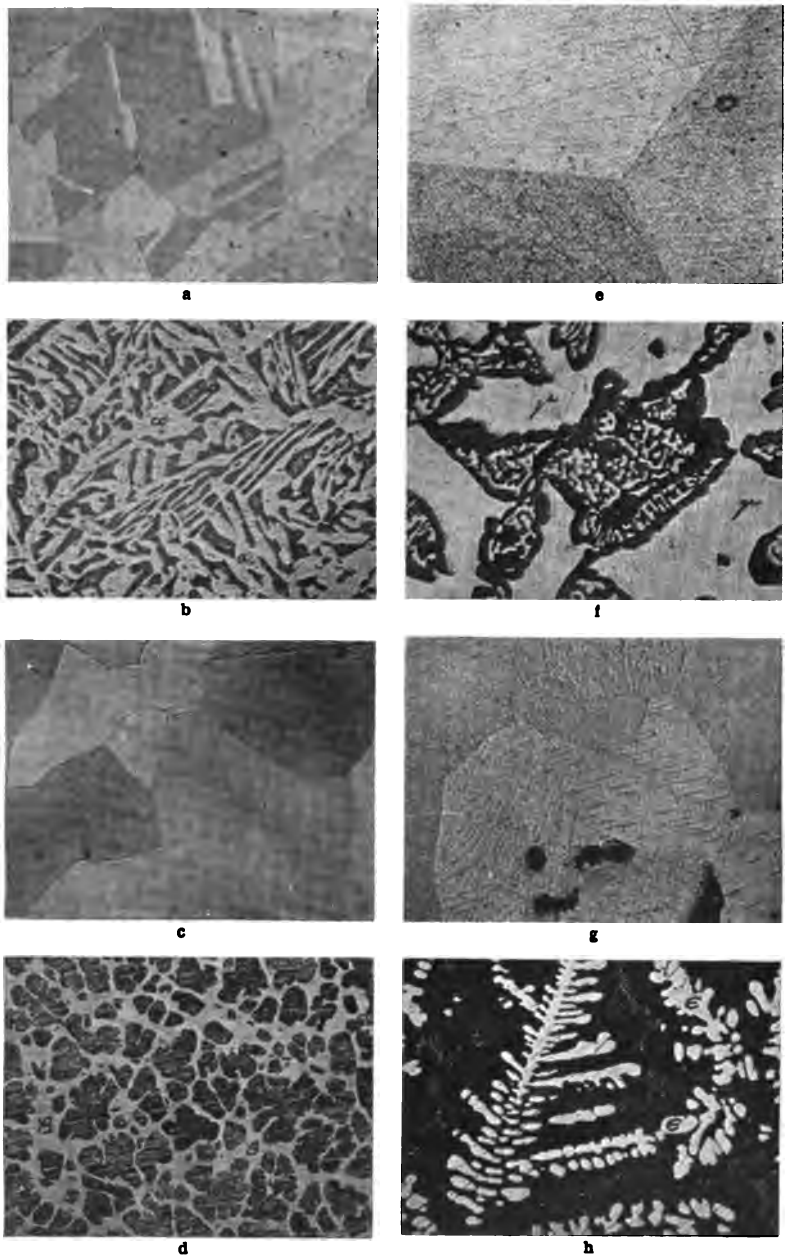


FIG. 14.—*Microstructure of the principal types of brasses, that is, alloys of the copper-zinc series.* × *100*

Note the alternation of alloys of simple and of duplex structure as the composition is varied. The alloys *d* to *h*, inclusive, are of very little use industrially. The approximate composition is indicated on the diagram, Fig. 13. (*a*) α brass, annealed after cold work, etched with acidified aqueous solution of ferric chloride; (*b*) α–β brass, hot-rolled, yellow matrix of beta containing reddish figures of alpha; etched with a dilute solution of sulphuric acid containing potassium dichromate; (*c*) β brass, cast, golden yellow in color, etched with an ammoniacal solution of copper ammonium chloride; (*d*) β–γ brass, cast, yellow matrix of beta containing silvery gray crystallites of gamma; etched with aqueous solution of ammonium persulphate; (*e*) γ brass, cast; silvery gray in color, hard and brittle; etched as in *d*; (*f*) γ–ε brass, cast; matrix of γ containing the eutectoid of γ and ε; etched as in *d*; (*g*) ε brass, cast, slightly purple when etched; etching reagent, ammonium hydroxide and ammonium persulphate; (*h*) ε–η brass, zinc-rich matrix of η containing bright unetched crystallites of ε; etched as in *d*

IV. CONDITIONS AFFECTING STRUCTURE

1. CHEMICAL COMPOSITION

Of all the factors which determine the structure of an alloy, chemical composition is without doubt the most important. Not only do alloys of entirely different composition differ in structure, but alloys of varying proportions of the same metals show structural variations according to the percentage composition which are often as marked as if they were composed of entirely different component metals. To discuss adequately these structural variations due to composition would necessitate a lengthy review of the subject of phase rule and the different classes of alloys on the basis of the constitutional diagram of the various systems. Such a review is neither necessary nor desirable here. A brief reference to the copper-zinc alloys will suffice to illustrate the point. In Fig. 13 is given the constitutional or structural diagram of this series, in which is shown the condition which obtains for every composition for temperatures from 0°C. up to that of the molten metal. In Fig. 14 micrographs of typical copper-zinc alloys are shown to illustrate the pronounced changes which occur in the structure at room temperatures as the composition is varied.

A similar set of micrographs is given in Fig. 15 to show the change occurring in annealed steel as the carbon content is progressively increased. It is evident from Fig. 15 that it should be possible to determine the carbon content of such material rather accurately from careful estimation of the amount of the carbon-bearing constituent present in the steel. Such a method is often used to supplement chemical analysis and to show the magnitude of variations in composition, which the ordinary method of sampling does not permit chemical analysis to detect.

As already mentioned in the discussion of the macrostructure of metals, segregation in steels is one of the most serious defects to which this class of metals is subject. The composition of the segregated portion of a steel article often differs widely from that of the unsegregated portions. This is shown in Fig. 16, which represents the structure of a streak of segregated metal from the center of a railhead and also the intermediate and the outer portions of the same. The need of an examination of the structure to supplement a chemical analysis in such cases is very evident.

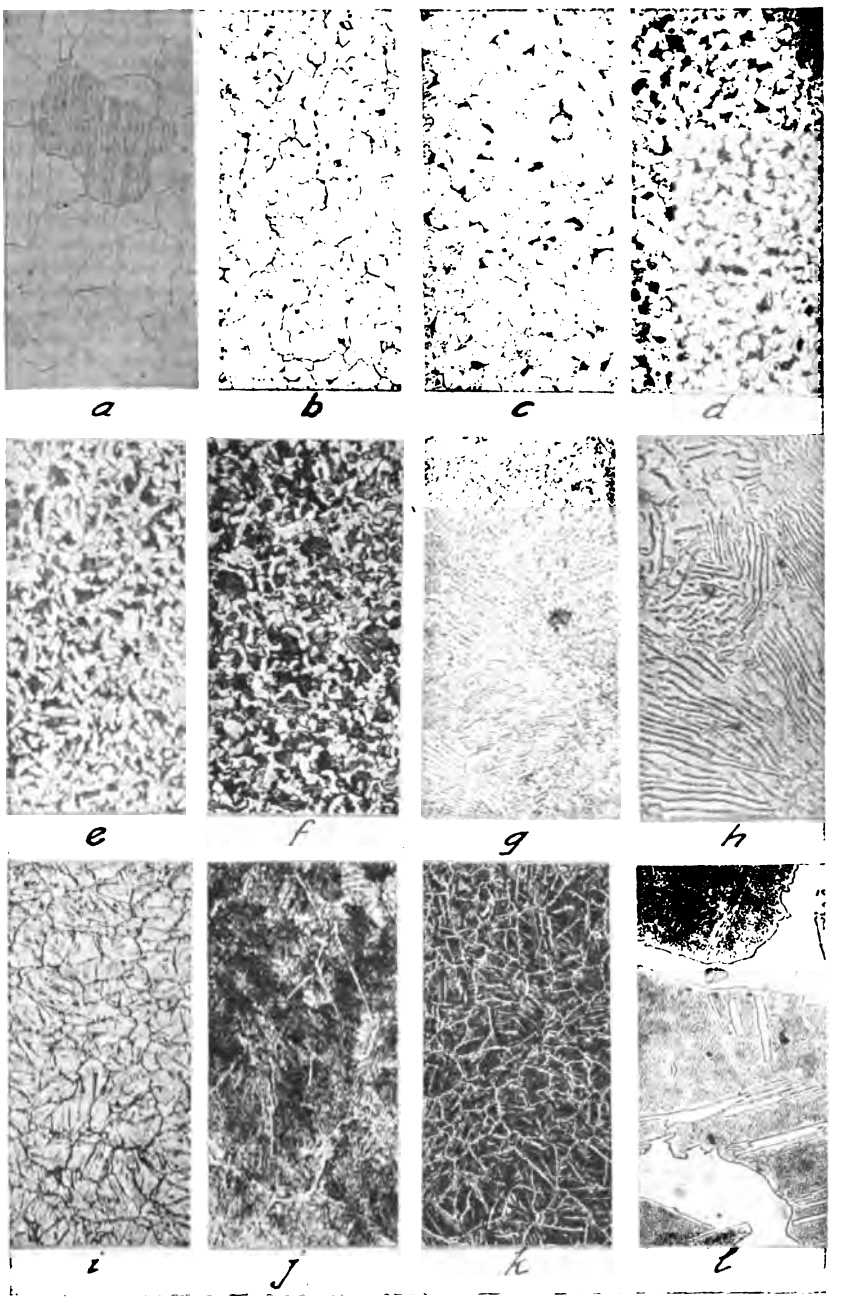


FIG. 15.—*Microstructure of typical annealed iron-carbon alloys (steels) illustrating the effect of variations in carbon content upon structure*

(*a*) Ferrite, electrolytic iron melted in vacuo. (*b*) to (*g*) Steels of ferrite-pearlite structure containing progressively increasing amounts of carbon as follows: *b*, 0.03 per cent; *c*, 0.07 per cent; *d*, 0.24 per cent; *e*, 0.32 per cent; *f*, 0.59 per cent; *g*, 0.68 per cent. (*h*) Eutectoid steel, 0.85 per cent carbon. (*i*) to (*l*) Steels of pearlite-cementite structure containing progressively increasing amounts of carbon as follows: *i*, 1.14 per cent; *j*, 1.14 per cent; *k*, 1.45 per cent; *l*, 1.70 per cent. × 100, except *g*, *h*, and *j*, × 500. Etching reagents, except for *i*, 2 per cent alcoholic solution of nitric acid, for *i* hot alkaline solution of sodium picrate

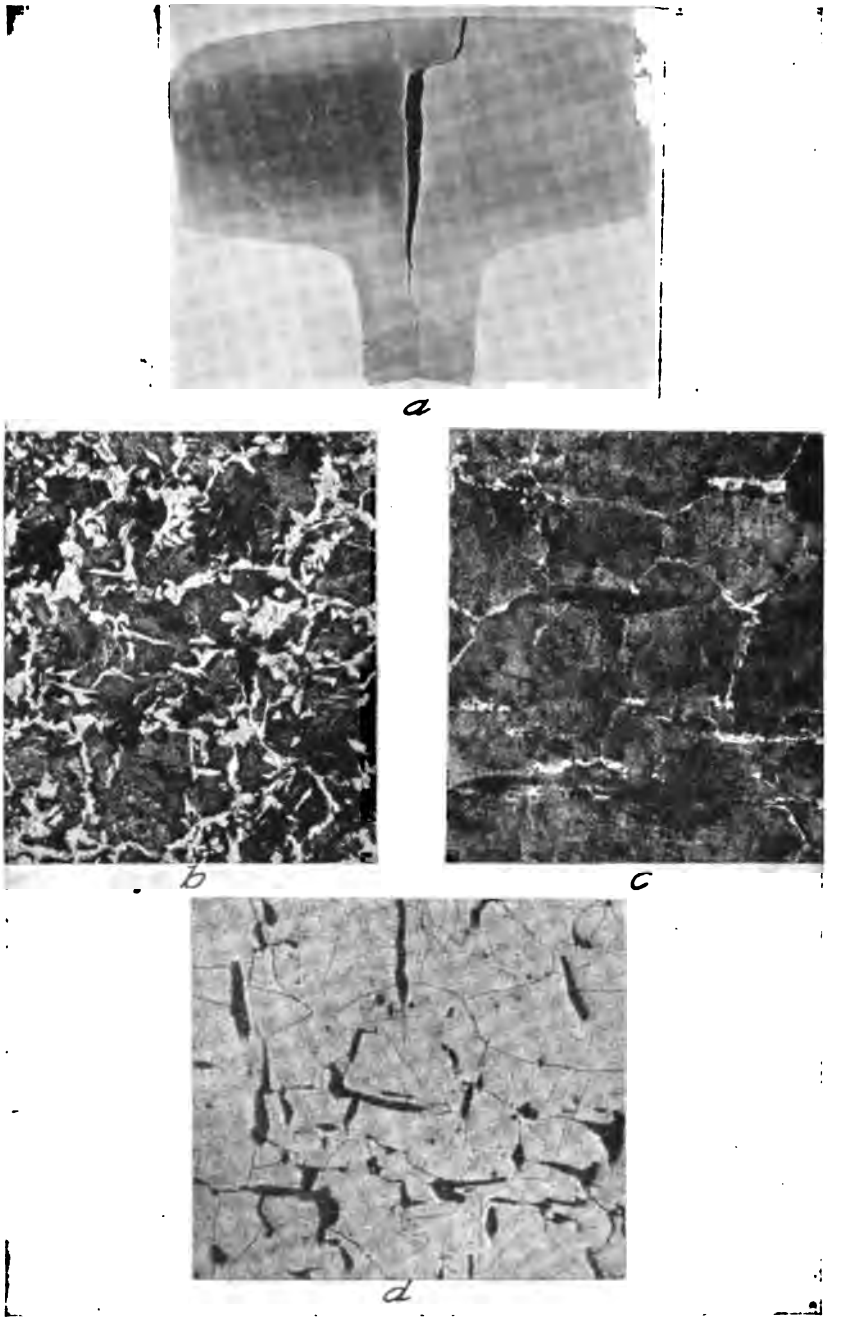


FIG. 16.—*Variations in the microstructure of rail steel caused by segregation*

The structure shown in *d* is indicative of very brittle material and the presence of this condition in the center of the rail head was responsible for the failure of the rail in service. (*a*) Cross section of head of rail which failed in service. × 1. (*b*) Structure of the steel comprising the greater part of the head, pearlite and ferrite. × 100. (*c*) Structure of steel from near the center of the head, pearlite with traces of ferrites. × 100. (*d*) Structure of the metal adjacent to the split which formed in the head, pearlite with films of cementite enveloping the grains. The metal was shattered by the formation of numerous intercrystalline cracks under the load to which it was subjected. × 100. Etching reagent: *b* and *c*, 2 per cent alcoholic solution of nitric acid; *d*, hot alkaline solution of sodium picrate

It may be noted in passing that this rail failed in service in the track, the fundamental cause being its abnormal segregation.

It often happens that metals and alloys show certain features of structure which are best described as being due to small inclosures of foreign material. Such inclosures, however, are often foreign only in the sense that they are not metallic. They are a necessary result of the metallurgical process used for the preparation of the material. The ever-present slag of wrought iron (Fig. 52) is an example. Such slag threads are characteristic of this material, and their presence or absence is often used as a criterion in disputed cases in deciding upon the nature of the material. The foreign inclosures may also result from additions made to the metal in course of preparation for improving its properties by some chemical reaction, for example, deoxidation and similar reactions. The products of the reaction are often retained in part by the metal after solidification and form a characteristic feature of the structure. Fig. 17 shows an inclusion in steel which resulted from an addition of titanium to the metal. The pink color and shape are quite characteristic of inclosures of this kind.

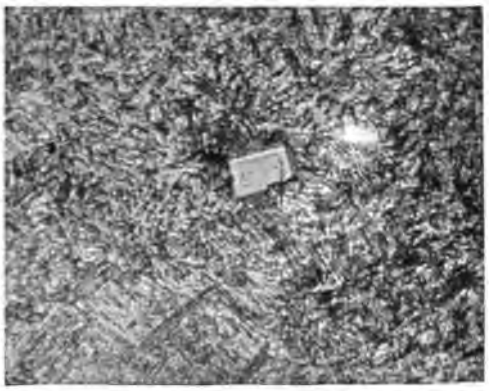


FIG. 17.—*Characteristic appearance of an inclusion caused by the addition of titanium to steel.* × 1000

Etching reagent, 2 per cent alcoholic solution of nitric acid

Some of the foreign inclusions are under certain conditions decidedly injurious to the metal in which they occur; that is, they cause its mechanical properties to be very inferior to what they would be otherwise. Sulphur in steel is a well known example of this. In the form of ferrous sulphide, because of the form in which it is distributed (as thin films enveloping the grains), it renders the steel almost unworkable at a red heat. This can be readily overcome, however, by the proper addition of manganese to the molten steel at the proper time. Fig. 18 shows the characteristic appearance of the sulphur in steel when in the form of ferrous sulphide and also when it has been converted into manganese sulphide. The inclusions of manganese

sulphide are not particularly harmful in the metal; that is, no more so than any similar inclusions are.

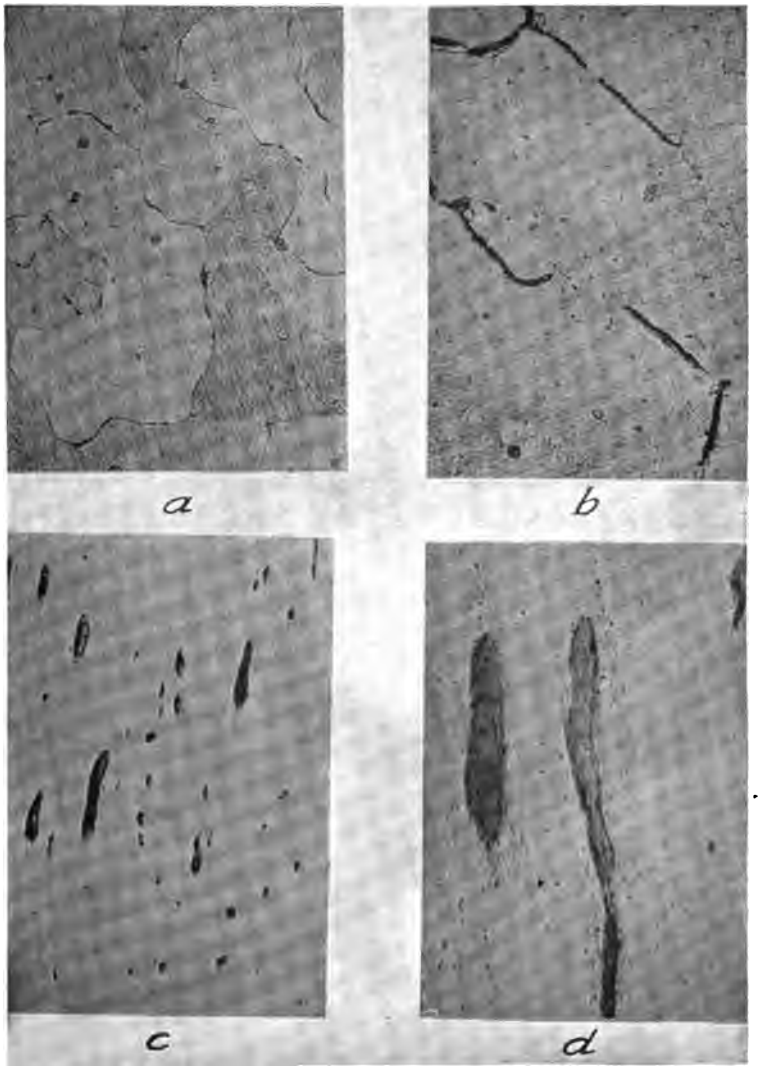


FIG. 18.—*Microstructure of low carbon steel, illustrating the forms in which sulphur may occur*

Note the dark-colored films enveloping the grains *a* and *b*. Sulphide in this form is very detrimental to the properties of steel. (*a*) Longitudinal section of the segregated center of a 2-inch round intended for chains; it was impossible to forge and weld the material satisfactorily on account of the films of ferrous sulphide enveloping the grains. × 100. (*b*) Same as *a*. × 500. Etching reagent, 2 per cent alcoholic solution of nitric acid followed by hot alkaline sodium picrate. (*c*) Longitudinal section of steel rod intended for use in automatic lathe. The sulphur is in the form of isolated globules of manganese sulphide. × 100. (*d*) Same as *c*. Specimen is unetched. × 500

A striking illustration of the effect of relatively slight changes in the chemical composition upon the structure of an alloy is af-

forded by cast iron. When slowly cooled from the molten state, the metal assumes the form commonly known as gray iron, a large proportion of its carbon being in the form of graphite. By chilling the metal when cast, the form known as white iron results, the metal being in a state of unstable equilibrium. In this case most of the carbon is retained in the combined form; that is, as cementite—the hard, brittle constituent. The relative silicon content of different cast irons has a pronounced effect upon the structure resulting, even where all are cooled at the same rate. It is a well-established fact that an increase of silicon favors graphitization; that is, induces stable equilibrium even with rather rapid cooling, while a low silicon content permits the alloy to retain the unstable condition. For this reason the silicon content of cast iron is purposely varied by the foundry man; for ordinary castings for which gray iron is desired, the silicon content is raised to a relatively high value, for example, 2 per cent and more. On the other hand, when a white iron is desired either for chilled castings to be used as such or for the production of malleable castings, the silicon content is kept relatively low, for example, approximately 0.50 per cent.

2. TEMPERATURE

The temperature to which a metal or alloy is heated, that is, after it has been formed, has in most cases a marked influence upon its structure. These structural changes dependent upon heating may be conveniently discussed under the following headings: Equilibrium changes, grain growth, and phase changes.

(a) EQUILIBRIUM CHANGES

Practically all metals and alloys when cast are far from being in a condition of structural equilibrium such as the phase rule predicates for the given conditions of composition and temperature. Although such conditions are often accentuated by rapid cooling during the process of casting of the alloy, slow cooling in itself does not necessarily result in structural equilibrium. Metals, unless exceptionally pure, and alloys normally show a cored or dendritic structure when in the cast state. This is a natural consequence of the selective process of freezing by which they solidify. In each crystal a branched or treelike core which is relatively rich in the element of highest melting point is first formed, and nonsoluble impurities collect, and constituents of lower melting point form in the interstices between the branches, the average composition of the material at such points being quite different

from that of the "core." Thus, every grain or crystal of the cast metal or alloy is nonhomogeneous in its composition, although the average composition of the whole grain is approximately that of the average for the alloy. Fig. 19 illustrates this condition. When an alloy showing such a "cored" structure is heated for a time

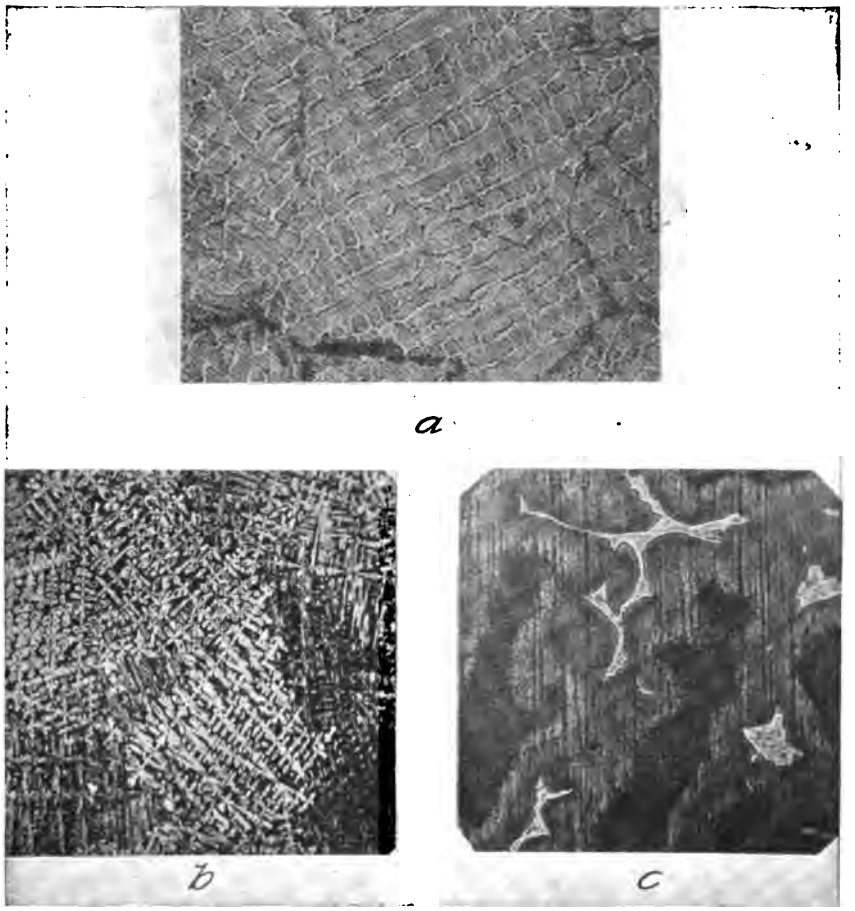


FIG. 19.—*Characteristic appearance of cast alloys, showing a dendritic structure*

(*a*) Nickel brass, a one-constituent alloy. × 100. The castings were defective on account of the intercrystalline cracks which formed during casting. Etching reagent, concentrated ammonium hydroxide. (*b*) Zinc bronze, a two-constituent alloy. Approximate composition: Copper, 88 per cent; tin, 10 per cent; zinc, 2 per cent; very slowly cooled from the molten state × 5. (*c*) Same as *b*. × 100. Etching reagent *b* and *c*, ammonium hydroxide and hydrogen peroxide

at a relatively high temperature, the principal effect is to erase the structural pattern by allowing diffusion to take place within the body of each crystal so that chemical homogeneity is approached. The changes which take place in a cast alloy upon heating are shown in Fig. 20, which represents a bronze as cast and similar

ones after prolonged heating. Unless such material has been subjected to other conditions, that is, straining by mechanical

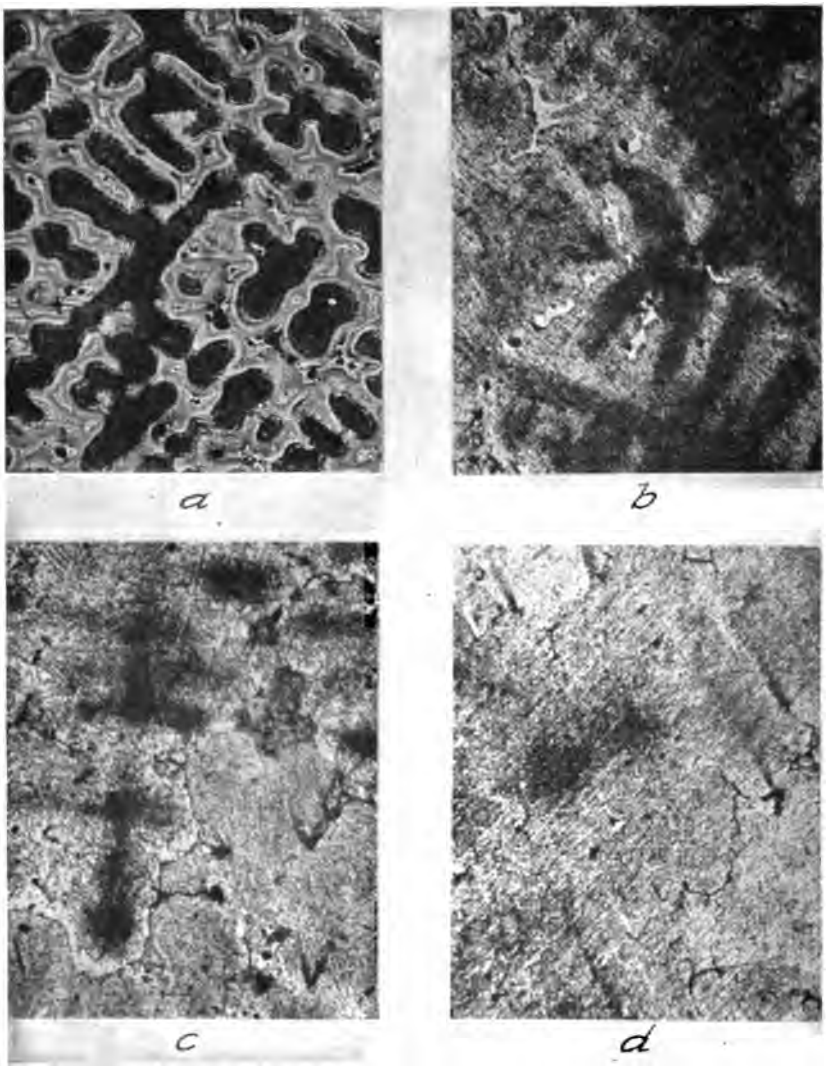


FIG. 20.—*Microstructural changes in a cast alloy caused by prolonged heating.* × 100

Note the gradual disappearance of the dendritic pattern as a result of annealing the cast alloy. (*a*) Cast zinc-bronze. Approximate composition: Copper, 88 per cent; tin, 10 per cent; zinc, 2 per cent. As cast, the alloy contains two constituents and has a pronounced dendritic structure. (*b*) Alloy similar to *a*, heated 8 hours at 400° C. Diffusion has taken place to some extent. (*c*) Alloy similar to *a*, heated 8 hours at 600° C. The eutectoid has been absorbed by the matrix, but the dendritic pattern is still obvious. (*d*) Another portion of specimen *c*; this portion of the alloy consists of an almost homogeneous solid solution. Etching reagent, ammonium hydroxide and hydrogen peroxide

deformation or its equivalent—excessively rapid cooling from a very high temperature, change of grain size in a cast alloy does not

take place upon heating. The principal effect of the heat upon the chemically nonhomogeneous cast material is to render it more nearly uniform in the composition by permitting diffusion and, in some cases, solution of certain constituents to occur, thus allowing chemical equilibrium to be brought about.

Other effects of heat upon the structure of alloys which may be briefly mentioned are the decomposition of a compound, as is illustrated by the formation of graphite from cementite during the heating of white cast iron and in some cases in high-carbon steels (Fig. 21), the mechanical break-up of eutectics and eutec-

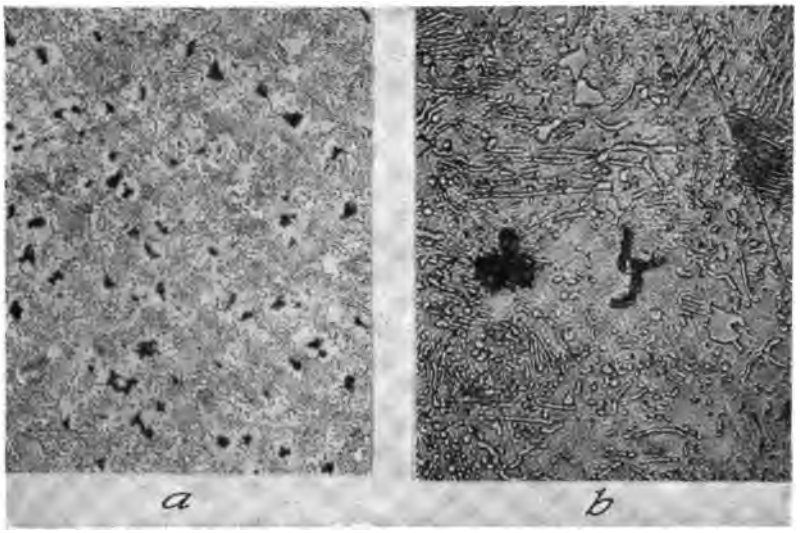


FIG. 21.—*Microstructure of high-carbon steel in which graphitization has occurred*

Each of the irregular black spots indicates the presence of graphite. Such steel is useless for the purpose for which high-carbon steel is generally employed. (*a*) Tool steel, 1 per cent carbon, showing specks of graphite which have formed at the expense of the combined carbon; each speck of graphite is surrounded by an area of ferrite; percentage of graphite, 0.51. × 100. (*b*) Same specimen. × 500. Etching reagent, 2 per cent alcoholic solution of nitric acid

toids by the coalescence of the different constituents under the action of heat, illustrated by the spheroidizing of pearlite by long-continued heating of steel just below the A_1 transformation temperature (Fig. 34). Other cases might be cited; the above are sufficient, however, to illustrate the typical changes which may occur.

(*b*) GRAIN GROWTH

The most striking change occurring in the structure of metals and alloys upon heating is the increase in grain size which often occurs. Such a change in grain size usually necessitates a preliminary straining of the material. Cast alloys, at least those

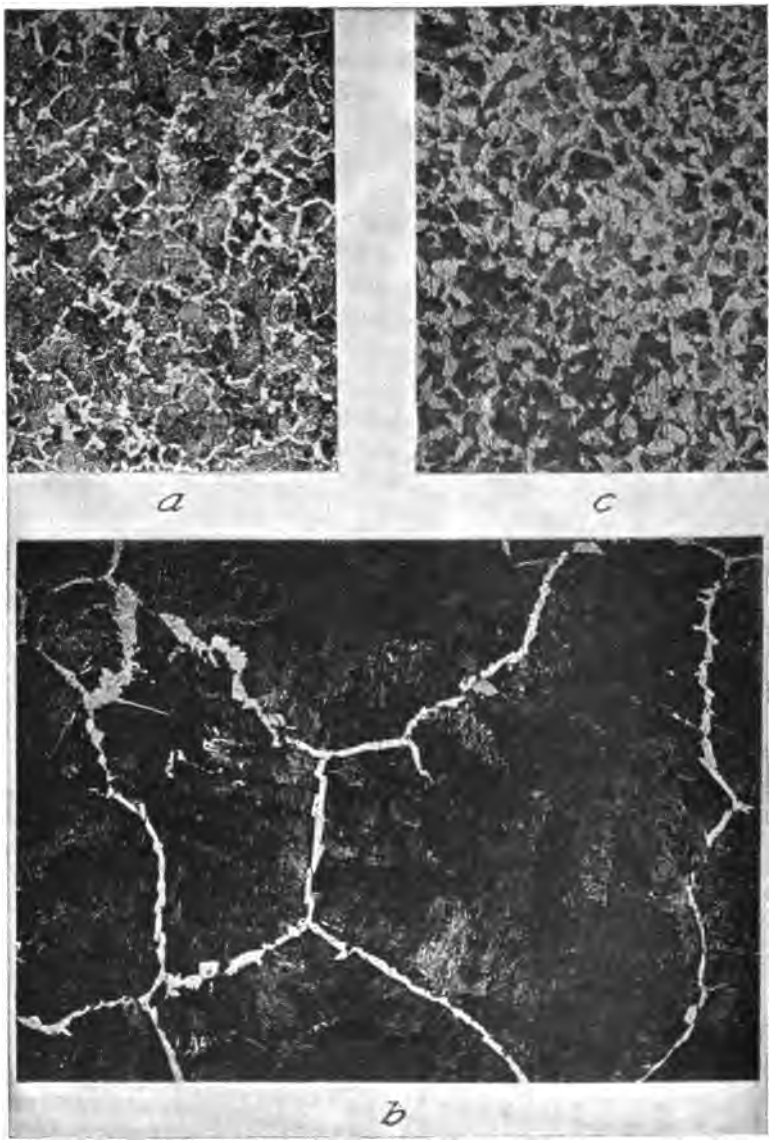


FIG. 22.—*Microstructure of 0.47 per cent carbon steel illustrating the structural effect of overheating and of grain refinement.* × 100

Note how the very large grains (*b*) may be replaced by much smaller ones (*c*) by proper annealing practice. The mechanical properties are correspondingly improved at the same time. (*a*) Material as received from the manufacturer. (*b*) Material similar to *a*, heated 6 hours at 1110° C (2030° F) and cooled in air. (*c*) Material *b*, reheated at 780° C (1440° F) for 3 hours and 45 minutes and furnace-cooled. Etching reagent, 2 per cent alcoholic solution of nitric acid

which involve no phase change upon heating, will show no increase in grain size even after several months heating,[15] unless the material has been strained in some way. Since so many metals and alloys are subjected to mechanical work of some kind in their fabrication or to other conditions in special cases which bring about grain growth upon subsequent heating, the fact is often lost sight of that grain growth is not the simple result of heating only, and that other conditions are necessary to bring it about. The latest opinions on this subject are given in the reference cited above.

Fig. 22 *b* shows the increase in grain size which resulted in a steel bar by improper annealing. The distortion of the material which occurred in the rolling of the metal as well as the fact that the material is subject to a phase change upon heating accounts for the pronounced grain growth which occurred upon heating. A coarsely grained condition in metals is usually regarded as very undesirable and particularly so in metals which may be subjected to shock or similar conditions in service. An investigation[16] under way at this Bureau has for its object the determination of the mechanical properties of steels which are most affected by variations in grain size of the material.

(c) PHASE CHANGES

In a great many alloys pronounced structural changes occur upon heating to certain definite temperatures which of course vary with the different alloys under consideration. Such changes are to be ascribed to phase changes or transformations within the material, such as are indicated in many of the constitutional diagrams for the various classes of alloys. By quickly cooling an alloy which exhibits such changes from a temperature somewhat higher than that at which the transformation occurs, the structure normally existing only at the higher temperature persists to a large extent in the material at room temperature, the alloy being in a state of unstable equilibrium.

This fact is of very great industrial importance; the art of heat treatment of alloys, particularly steel, for high mechanical properties depends upon this fact. Fig. 23 shows the structure of a low-carbon steel as usually observed and the structure of the same as it exists at a temperature somewhat above the first or A_1

[15] H. C. H. Carpenter and C. F. Elam, "Grain growth and recrystallization of metals," J. Inst. of Metals, 24, 1920.

[16] H. S. Rawdon and Emilio Jimeno-Gil, The Relation of Brinell Hardness to the Grain Size of Annealed Carbon Steels, B. S. Sci. Papers, No. 397.

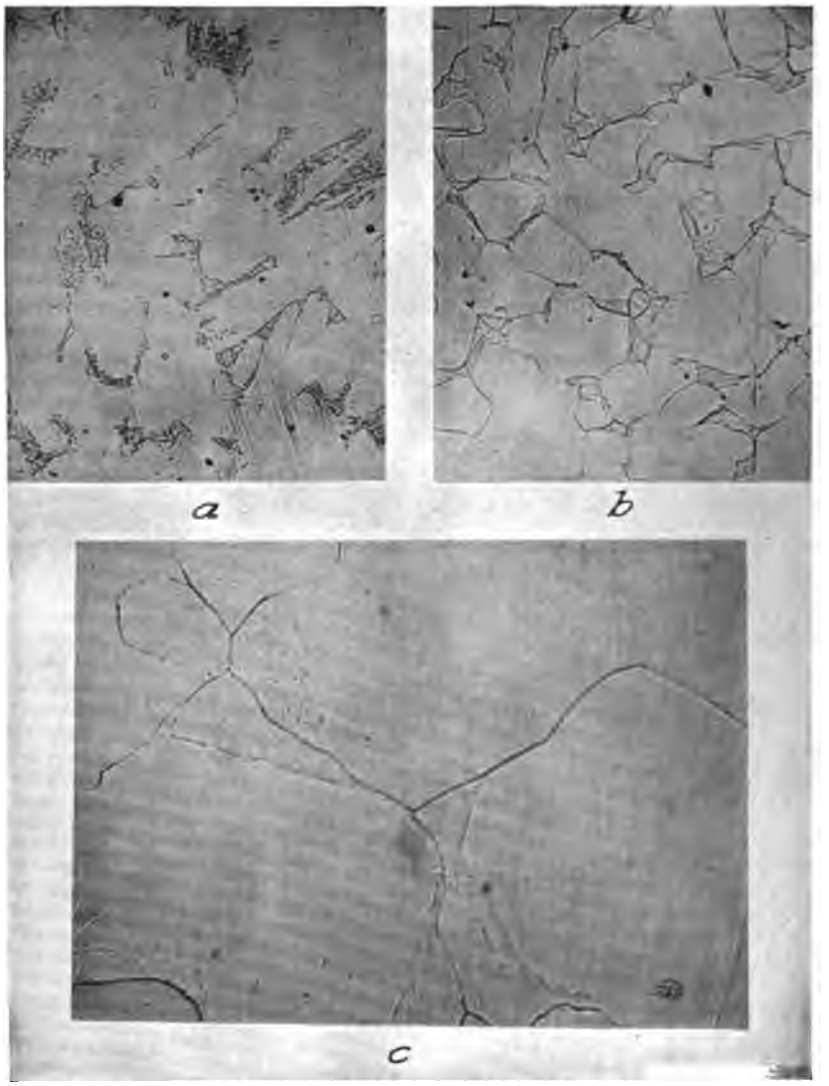


FIG. 23.—*Microstructure of 0.18 per cent carbon steel as it exists at ordinary temperatures and at relatively high temperatures*

(*a*) Pearlite-ferrite structure of the material at ordinary temperatures, revealed by etching with 2 per cent alcoholic solution of nitric acid. × 100. (*b*) Same specimen as *a*; high-temperature structure revealed by heating the polished specimen in vacuo 30 minutes at 750° C (above the A_1 transformation), and cooling in vacuo. A pronounced volume change, which is opposite in its character to that caused by heat alone, occurs in the steel during its transformation at the critical temperature. The deformation of the polished surface due to this change in volume reveals the extent to which the austenitic solid solution resulting from the transformation of the pearlite merged with the ferrite matrix. × 100. (*c*) Same as *b*, × 500

transformation, as recorded by a special method of heat etching by heating the polished specimen in vacuo. By quickly cooling the steel, for example, by quenching, from the temperature at

which the "high-temperature structure" was examined, the structural condition obtaining at that temperature would be maintained in the quickly cooled alloy; pronounced changes in its physical properties would result from the new structural conditions. Fig. 71 illustrates the same phenomenon in a non-ferrous alloy.

The phase changes or transformations in alloys are accompanied by energy (heat) manifestations. Hence it is much easier to investigate and establish the temperatures at which the changes

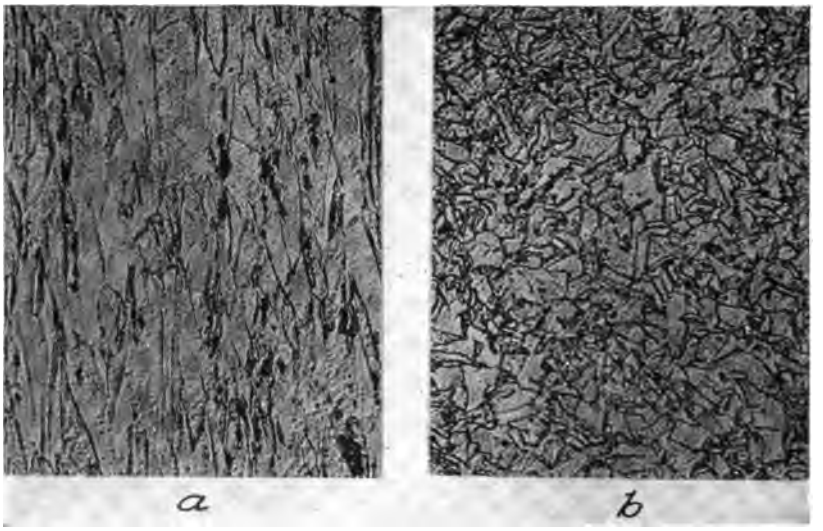


FIG. 24.—*Microstructure of cold-drawn copper, showing the mechanical distortion as revealed by sections parallel to and perpendicular to the direction of working.* × 250

Note the difference in the grains of *a* and *b*; the mechanical properties differ in the longitudinal and transverse directions in a manner corresponding to the difference in structure. (*a*) Longitudinal section of ½-inch trolley wire; (*b*) Cross section of same. Etching reagent, concentrated ammonium hydroxide and hydrogen peroxide

occur by the relatively simple means of "thermal analysis" rather than by the tedious and complicated methods necessary for the determination of the high-temperature structure of the material. Thermal analysis may be regarded then as the means for demonstrating the structural changes which occur in alloys upon heating as well as the energy changes which accompany them. It may be noted, however, that some energy changes have been observed for which any possible accompanying structural change is so minute as to be beyond the range of the methods now used for observing the structure of metals.

3. WORKING OF METALS

(*a*) DISTORTION OF CRYSTALLINE STRUCTURE

One of the most potent factors affecting the structure of metals and alloys is the amount of mechanical working received during

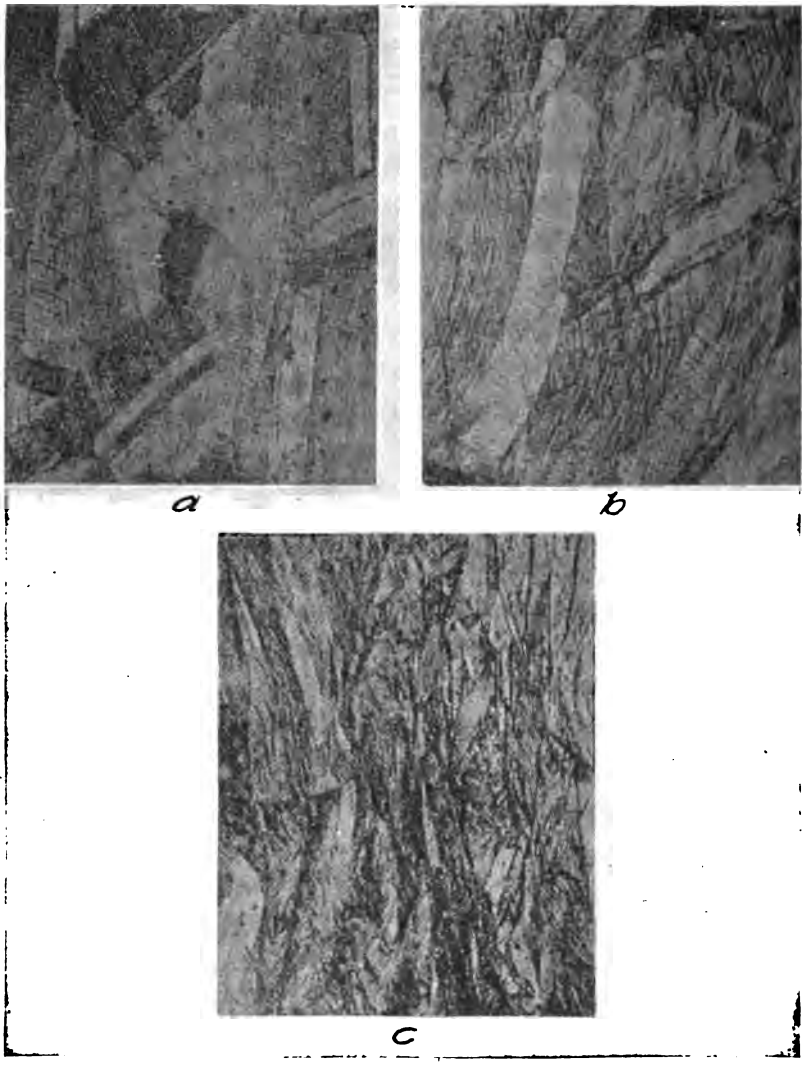


FIG. 25.—*Microstructure of brass illustrating progressive stages in the crystalline distortion produced by cold-working* × 100

Note the series of parallel lines within the different grains. The hardening of brass by cold-working it is the result of the changes occurring within the individual crystals, as indicated by these lines. (*a*), (*b*), and (*c*) show three stages in the crystalline distortion of cartridge brass (approximate composition, copper, 70 per cent; zinc, 30 per cent) by cold working the alloy. The series of parallel lines within any one crystal represent the planes along which the metal "slips." Etching reagent, ammoniacal solution of copper ammonium chloride

fabrication after casting. Aside from the part played by the straining of metals in causing recrystallization and grain growth upon subsequent heating as explained above, the structure of the metal is often profoundly changed by the deformation of the material. Thus sections of a metal parallel to the direction of working will differ very materially in their appearance from those perpendicular to the same. Such sections are conveniently designated as longitudinal and transverse sections, respectively. In Fig. 24 two such sections of cold-drawn copper are shown to illustrate the structural change which accompanies mechanical working.

FIG. 26.—*Microstructure of annealed cast bronze showing the thickness of the surface layer of cold-worked metal.* × 100

A specimen of cast zinc bronze (approximate composition, copper, 88 per cent; tin, 10 per cent; zinc, 2 per cent) was turned in the lathe and afterwards heated at 600° C for 2 hours. The distorted metal at the surface recrystallized under this treatment, the cast metal of the center did not. Etching reagent, alcoholic solution of ferric chloride

As is to be expected, if the deformation or working has been carried out upon the cold material, the distortion of crystalline structure will be much more severe than if carried out upon the metal while hot. Thus, thin cold-rolled sheets and fine cold-drawn wires, particularly of the softer metals and alloys, appear practically "structureless" when examined by the usual metallographic methods. Excessive cold working of the surface of harder metals, for example, steels, will sometimes result in the formation of a hard "structureless" surface layer. The accompanying temperature effect due to the heat of friction may also contribute in such cases.

In Fig. 25 is shown a specimen of cartridge brass (approximately 70 per cent copper, 30 per cent zinc), which has been rather severely cold worked. This illustrates how the deformation or change of crystal form is brought about by means of internal slips or "faulting" along definite planes within the individual crystals. These "faults" persist in the crystals and are revealed when the metal is etched; they are not to be regarded necessarily, however, as discontinuities within the crystals. As the metal is more severely worked, these slips become so numerous that they fill

the entire elongated grain and are no longer to be observed with certainty.

The depth to which a metal (cast) has been distorted by cold-working, for example, in machining operations, can often be detected by making use of the fact that upon heating recrystallization of the cold-worked metal will occur. Fig. 26 shows a specimen of cast bronze[17] which was turned to size and shape in the lathe. Upon annealing a specimen, the depth to which the distortion of the material extended was clearly shown by the thickness of the recrystallized layer.

V. EFFECTS OF STRUCTURE UPON PROPERTIES

The ultimate aim of any metallographic examination is to show in what manner and to what extent the characteristics of the material, particularly the mechanical properties, are dependent upon the particular features characterizing the structure of the metal under observation. To discuss here this phase of the subject, even in a manner only approximately complete, is impossible. Only a few of the most obvious effects of structure upon the properties will be mentioned.

1. MECHANICAL PROPERTIES

It must be borne in mind in a discussion of this subject that the mechanical properties of any material, as expressed numerically, are more or less dependent upon the method of determination used, for example, size and shape of test specimen, rate at which the stress is applied, etc. The structural features of the material are closely related to the mechanical properties, this relationship, of course, being much more apparent in the case of the grosser or macroscopic features than for the very minute characteristics, as will be evident in the following examples which are discussed. The previous treatment, mechanical as well as thermal, also affects the mechanical properties, although in this case it may be contended that the structural effects caused by the previous treatments are largely, if not entirely, responsible for the changes noted.

(*a*) HARD AND SOFT CONSTITUENTS

Many of the alloys most useful from the industrial standpoint consist of two or more constituents which vary very widely in their characteristics. One of the constituents is often relatively

[17] H. S. Rawdon, Microstructural Changes Accompanying the Annealing of Cast Bronze, B. S. Tech. Papers, No. 60.

very soft and ductile, while a second is hard and brittle. For example, such a condition occurs in steels, in aluminum casting alloys, and in bronzes, particularly those for bearing purposes. The softer constituent gives the required ductility, while stiffness and strength are contributed by the harder one, which is disseminated throughout the soft matrix. The relative proportions of the two determine the properties of the alloys of the same general series which differ among themselves in their percentage composition.

Fig. 27 shows a specimen of cast zinc bronze (approximately 88 per cent copper, 10 per cent tin, and 2 per cent zinc) which was stressed in tension until fracture occurred. The soft ductile copper-rich matrix easily adapted itself to the applied loading, the hard, brittle tin-rich constituent was shattered and broken, as shown, when stressed sufficiently. Similar cases may be noted in other alloys. Fig. 28 shows a portion of a test specimen of an aluminum-casting alloy broken in tension. The hard constituent, consisting of a compound of aluminum and copper ($CuAl_2$), was sufficient in amount to form a continuous network throughout the alloy. The course or path of the fracture of a test specimen was determined by this network, as is shown in Fig. 28; thus the results of a tension test of such a material depend primarily upon the amount and the properties of this constituent.

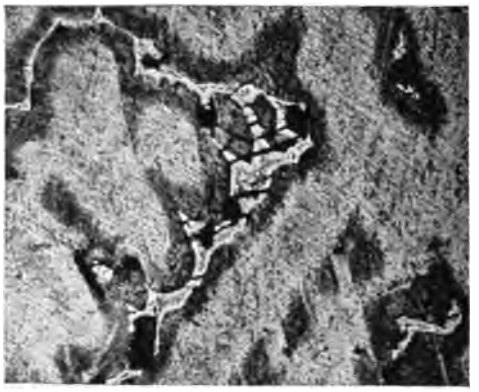


FIG. 27.—*Microstructure of cast zinc bronze which has been stressed in tension.* × *250*

Note the parallel black lines in the light-colored constituents. These are cracks which formed in the brittle constituent at right angles to the direction in which the stress was applied. Approximate composition of alloys, copper, 88 per cent; tin, 10 per cent; zinc, 2 per cent. Etching reagent, concentrated ammonium hydroxide

(*b*) SOFT DUCTILE CONSTITUENTS

Copper and lead do not alloy with each other in the sense that most metals do; neither solid solutions nor definite compounds of the two are formed. An "alloy" of these metals consists only of a mechanical mixture of the two metals, the intimacy of the mix depending largely upon the care used in preparation and the

skill of the operator. The "alloy" may be considered, for convenience, as a copper sponge, the interstices of which are filled with globules of lead, as is shown in Fig. 29.

Although both copper and lead when reasonably pure are highly ductile, the mixture of the two behaves in a rather anomalous manner when tested. The behavior of the material when stressed in tension is somewhat as might be expected. It is somewhat ductile, but is decidedly inferior to metallic copper in its properties. Thus a tension test of an alloy consisting essentially of 40 per cent lead and 60 per cent copper gave the follow-

FIG. 28.—*Microstructure of cast aluminum alloy showing the "path" of the fracture produced by a tensile stress.* × *100*

The alloy was of the following approximate composition: Copper, 1.8 per cent; magnesium, 1.7 per cent; manganese, 1.2 per cent; aluminum, remainder. Such an alloy consists of a framework of a hard constituent embedded in a much softer matrix. Note that the "path" of the fracture in tension was determined largely by the framework of the hard constituent. This has been indicated by arrows. Etching reagent, 0.1 per cent solution of sodium hydroxide

ing results: Ultimate strength in tension, 10 650 pounds per square inch; elongation in 2 inches, 8.5 per cent; and reduction of area, 7.5 per cent. The continuity of the copper matrix is so broken up and weakened by the inclosed globules of lead, which of course are of very low tensile strength, that the resulting tensile properties are correspondingly lowered. The properties measured are essentially those of the copper sponge, and the properties of any particular specimen are inferior to those of a specimen containing the same amount of copper in the form of a solid, but smaller, rod.

The appearance of the fractured specimen of the "alloy" when tested in compression is shown in Fig. 29 *c*. Although each of

the two constituents is decidedly ductile under compression, the mixture of the two behaves in a manner characteristic of a brittle material. Instead of flattening to any appreciable extent, the

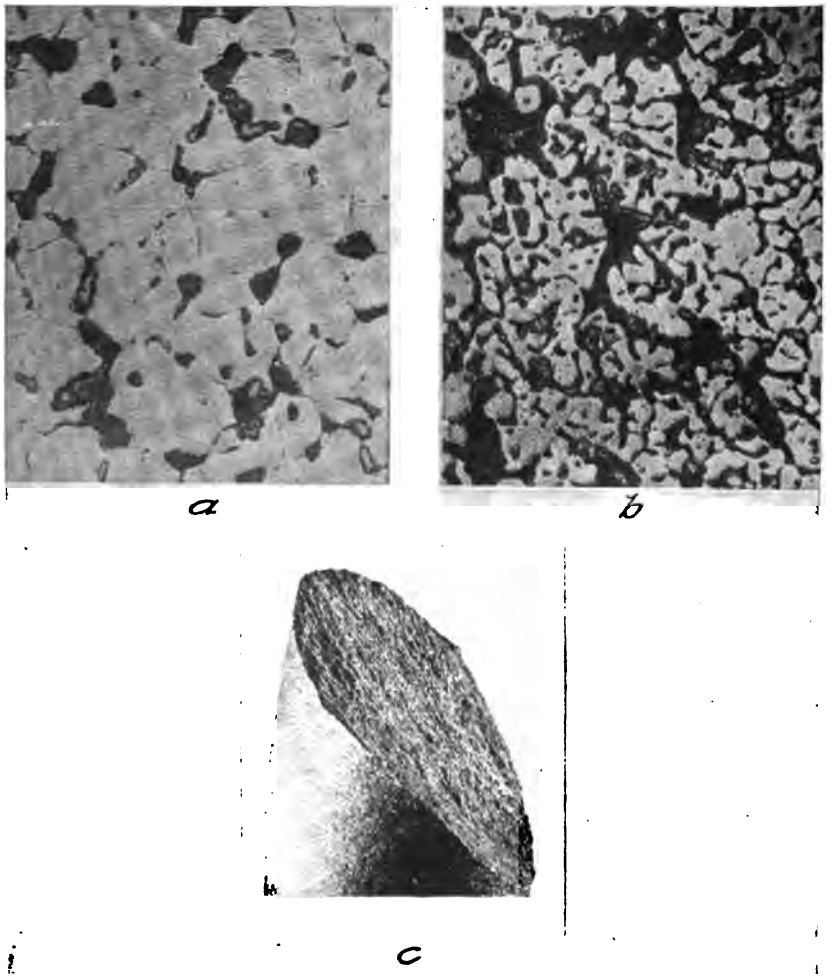


FIG. 29.—*Microstructure of copper-lead alloys and appearance of a specimen of the same after testing in compression*

"Alloys" of copper and lead consist simply of a mechanical mixture of the two metals. Note the black spots and network which indicate the spaces initially filled with globules of lead, traces of which still remain in place after the polishing of the specimen. The samples were slightly etched with concentrated nitric acid for developing the structure. (*a*) Alloy of approximate composition, copper, 77 per cent; lead, 23 per cent. × 100. (*b*) Alloy of approximate composition, copper, 60 per cent; lead, 40 per cent. × 100. (*c*) Compression specimen of alloy *b* after test. × 1. Note that the specimen sheared when compressed sufficiently in a manner considered characteristic of brittle alloys although each of the two component metals, copper and lead, is very ductile under compression

specimen shears in a manner such as is expected, for example, in cast iron. The inclosed globules of the lead undoubtedly contribute largely to the failure of the specimen in the manner shown,

by their action as a "lubricant." The ultimate strength in compression of lead is very much lower than that of copper; thus the lead yields under the applied loading and "flows" long before the copper is stressed to a degree which would cause appreciable deformation.

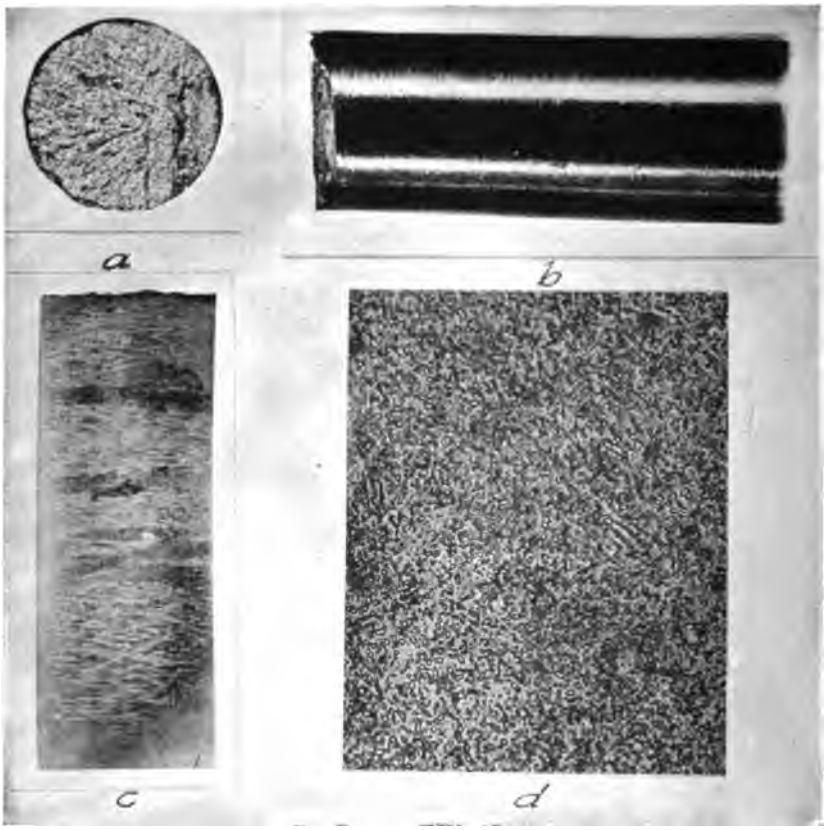


FIG. 30.—*Characteristic fractures of gun steel tested in tension across the grain of the metal, together with structure of the same*

Note the lack of elongation in the specimen *b* after test. The banded structure shown in *c* is largely responsible for this. (*a*) Face of the fracture of the tension specimen shown in side view in *b*, slightly less than × 2; (*c*) longitudinal medial section of *b*, etched with aqueous solution of copper ammonium chloride, slightly less than × 2; (*d*) Microstructure of specimen *b*, × 500. Etching reagent, 2 per cent alcoholic nitric acid

(*c*) ORIENTATION OF TEST SPECIMEN WITH RESPECT TO MATERIAL TESTED

It has been shown in a previous section that the mechanical working which is necessary for forming a metal after casting affects the structure to a very marked extent. The worked material has a more or less "fibrous" structure, depending largely upon variations in composition across a section of the ingot used

and particularly upon the various inclusions within the metal. After the working of the metal these are arranged in rather definite lines, the course of which is determined by the shaping of each particular piece.

It is evident that the mechanical properties when measured *across* a laminated or fibrous material will be quite different from those of the same material, the test specimen of which was cut

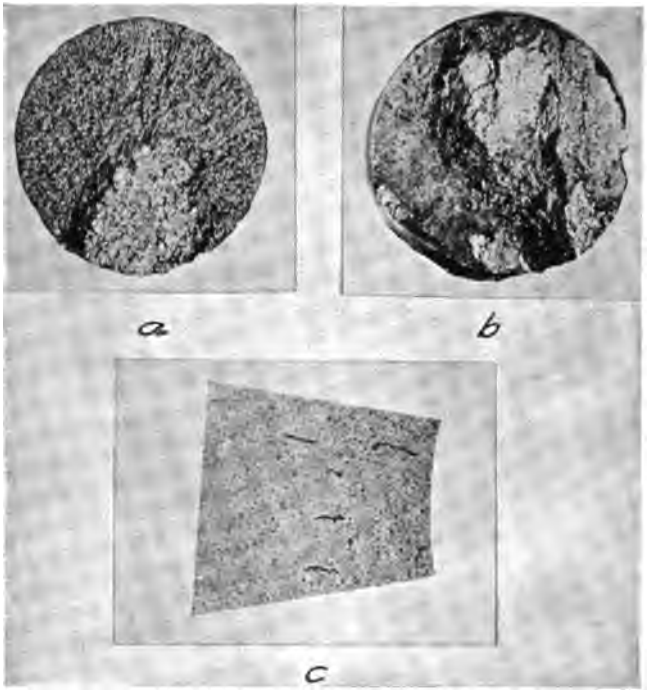


FIG. 31.—*Characteristic appearance of "flakes" in gun steel revealed by tensile fractures and macroscopic appearance of flaky steel*

Note the white areas, *a* and *b*. These correspond to the defects (discontinuities) of *c*. (*a*) and (*b*) Fractured faces of tension specimens of flaky steel. × 2. The "flakes" have a characteristic silvery appearance and the metal appears coarsely crystalline at such spots; microscopic examination, however, shows that the grain is the same across the entire cross section of the specimen. (*c*) Specimen of flaky gun steel deeply etched with concentrated hydrochloric acid. × 1. The acid widens and deepens the discontinuities (flakes)

parallel to the course of the fibers. In the latter case, which covers by far the greater majority of the test specimens used in industrial testing, the mechanical properties are not seriously affected. It is only when it is specified, as is done in some particular cases, for example, gun forgings, that the test specimen shall be cut transversely to the direction of working, that the effect is marked. Fig. 30 shows the appearance of a specimen of gun steel (carbon, 0.48 per cent; manganese, 0.76 per cent; nickel, 2.85 per cent;

sulphur, 0.02 per cent; phosphorus, 0.02 per cent) broken in tension, the following results being obtained: Yield point (by divider method) 79 000 lbs/in.^{2}; ultimate strength, 83 000 lbs./in.^{2}; reduction of area, 3.5 per cent; elongation in 2 inches, 3.5 per cent. The very marked banded structure of the material, which macroscopic examination showed was caused by threads of inclusions, is unquestionably the reason for the very low ductility shown by the material. From the microstructure of this material (Fig. 30 *d*) one has reason to expect that considerable ductility would be shown.

In Table 2 are summarized the results obtained by testing duplicate transverse and longitudinal specimens of the same material in tension. The metal chosen was a type of defective steel, encountered particularly in gun forgings, which has been designated as "flaky steel," of a composition very similar to that given above. Agreement among metallurgists as to the origin of these defects, "flakes," has not yet been reached. Their appearance as revealed by a tension break is shown in Fig. 31; deep etching of such steel in concentrated acid reveals their presence, as is shown in the same figure.

TABLE 2.—Tensile Properties of Flaky Steel as Revealed by Transverse and by Longtitudinal Test Specimens

Specimen	P-limit	Yield point	Ultimate strength	Reduction of area	Elongation in 2 inches	Modulus of elasticity
	Lbs./in.^{2}	Lbs./in.^{2}	Lbs./in.^{2}	Per cent	Per cent	Lbs./in.^{2}
Transverse	53 500	56 100	59 200	1.5	1.5	29 000 000
Do	65 000	67 000	92 950	5.0	3.5	29 000 000
Longitudinal	62 500	65 000	106 500	52.0	26.5	29 500 000
Do	62 500	65 000	106 850	50.5	26.0	29 500 000

It is very evident from the results given that the relation which the test specimen bears to the parent material affects the measured mechanical properties of the material to a marked degree. Defective material of the type used when tested in the ordinary manner shows apparently very superior properties, particularly in ductility. However, when a specimen cut transversely from the material is tested, it behaves very differently and breaks with practically no ductility. The elastic properties are not seriously affected, however, even when the internal defects are sufficient to reduce the ultimate strength of the material to approximately only 50 per cent of the normal value. When such material is

subjected to some of the dynamic methods of testing, impact, fatigue, etc., the difference in the results obtained for the transverse specimen is usually even more marked than the results given above for the tension test.

(*d*) COARSELY GRAINED METALS

It has been previously suggested that the grain size of a metal has a pronounced effect upon many of the properties of the material. Coarsely grained metals are quite universally regarded with disfavor, although there appears to be no evidence at hand to demonstrate the unsuitability of such material for many purposes. The brittleness usually attributed to large grain size is not very well revealed by a tension test, at least as ordinarily carried out. Fig. 32 shows a section of coarsely grained tension specimens of cast bronze. The structure indicates that the mechanical properties were determined to a very large degree by the fact that the entire cross-sectional area at the point at which the fracture occurred comprised only a few large grains. There was nothing however, to indicate this until the specimen was sectioned and its structure examined. A shock or impact test reveals the effect of coarse grain in a much more striking manner. Fig. 33 shows the appearance of two specimens of the same steel after testing in a

FIG. 32.—*Macrostructure of tension specimens of cast zinc bronze showing the relation of the fracture produced to the crystalline structure.* × 3

Note the very large grain size of both specimens. (*a*) and (*b*) Longitudinal medial sections through the fractured ends of two tension specimens of cast bronze (approximate composition, copper, 88 per cent; tin, 10 per cent; zinc, 2 per cent). In both specimens the path of the fracture was transcrystalline. The specimens were etched with alcoholic solution of ferric chloride and then covered with a coating of shellac

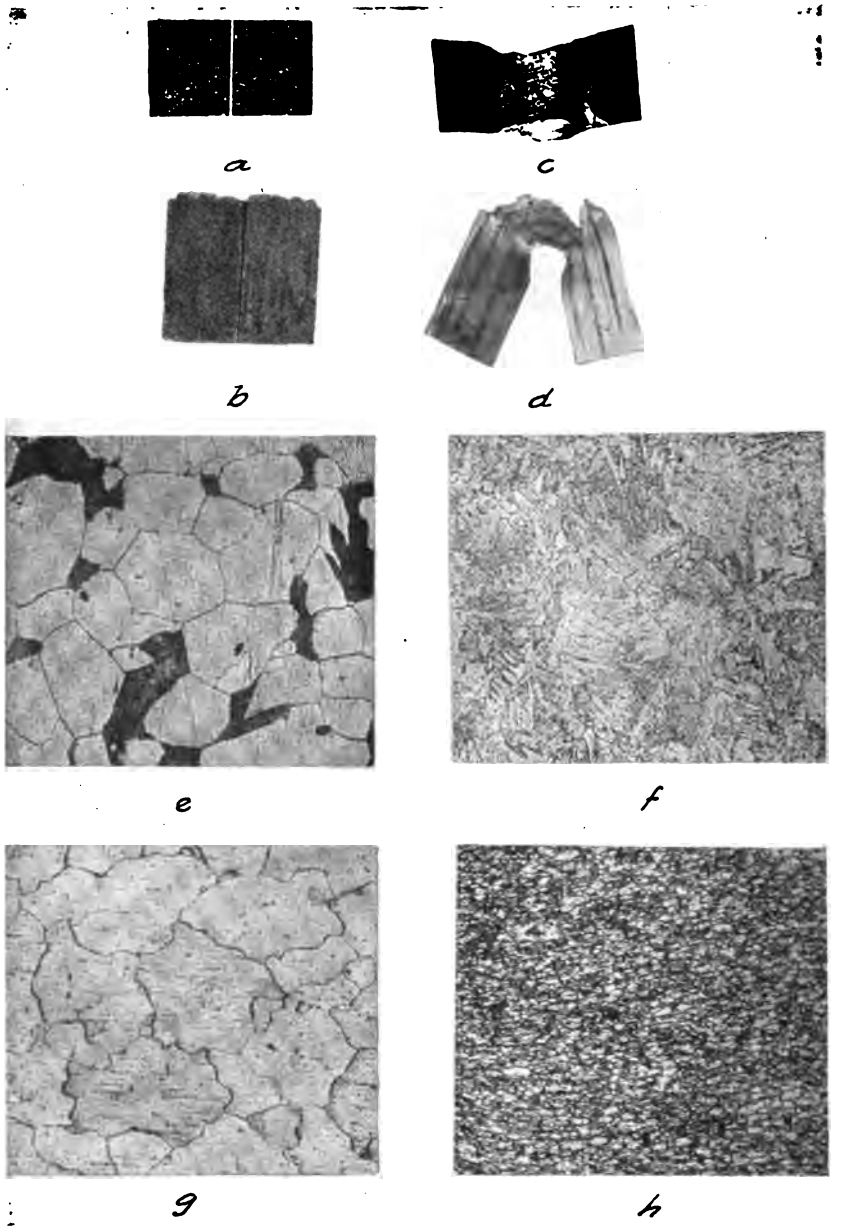


FIG. 33.—*Appearance of specimens of low-carbon steel with different thermal treatments showing the relation of impact properties to the microstructure of the material*

(*a*) and (*b*) Fractured face and side view of specimen of low-carbon steel broken by the Frémont impact test of a falling weight. × 1½. (*c*) and (*d*) Fractured face and side view of a second specimen of the same material tested in same way. × 1½. (*e*) Microstructure of specimen of *a–b*. × 100. The steel has been rendered coarsely grained evidently by overheating in the annealing process. (*f*) Microstructure of specimen *c–d*. × 100. Etching reagent, 2 per cent alcoholic solution of nitric acid. (*g*) Microstructure of soft iron wire (very low-carbon steel) which was as "brittle as glass" when an attempt was made to bend it at the temperature of liquid air. × 100. (*h*) Microstructure of a wire of similar composition which proved to be very tough at the temperature of liquid air and withstood several complete bends, 180°, before breaking. × 100. Note the difference in grain size of the brittle material *e* and *g* as compared with similar metal in the tough condition, *f* and *h*

Frémont impact testing machine; one of the specimens was spoiled evidently in the annealing process; the second, on the other hand, showed exceptionally superior qualities. The microstructure suggests that the superior shock-resisting properties were undoubtedly produced by quenching the steel from a high temperature, probably above that of the A_3 transformation. The entire lack of ductility of the coarsely grained specimen as compared with the superior shock-resisting qualities of the same steel when properly treated affords striking evidence of the influence of grain size upon mechanical properties. Fig. 33, *e* and *f*, illustrates the fact that at extremely low temperatures the grain size of metals is a factor of even greater importance in determining the mechanical properties than at ordinary temperature.

(*e*) PHYSICAL STATE OF MICROSCOPIC CONSTITUENTS

The relative size, arrangement, and method of distribution of the various constituents which make up the structure of an alloy bear a close relationship to the various properties of the alloy. This is best noted in a binary alloy, for example, eutectoid carbon steel, different specimens of which have been subjected to various thermal treatments with the express purpose of producing the variations in the microstructural features suggested above. Of course precautions must be taken that no phase changes in the alloy occur and that it is in stable equilibrium throughout, the differences produced in the structure being physical ones only.

Considerable investigational work has been done to show how the mechanical properties of carbon steels, particularly those of eutectoid composition, vary with the physical state of the pearlite, the steel being in the softened state throughout and the pearlite ranging from the lamellar type through various stages to the completely "divorced" or spheroidized condition. The work of Hanemann [18] and that of Howe [19] may be cited as illustrative of this.

The influence of the physical state of the pearlite in steel upon the properties is well shown by a study of the magnetic characteristics of the same steel after various treatments.[20] The various specimens of the steel (carbon 0.85 per cent; manganese, 0.28 per cent) were cooled from the same temperature (800° C) at rates so chosen that the structure of the different specimens varied from a

[18] H. Hanemann and F. Morawe, Über den körnigen Perlit und seiner Bedeutung für die Wärmebehandlung des Stahls, Stahl und Eisen, **33**, Part 2, p. 1350; 1913.

[19] H. M. Howe and A. G. Levy, "Notes on pearlite," J. Iron and Steel Inst., **94**, p. 210; 1916.

[20] C. Nusbaum and W. L. Cheney, B. S. Sci. Papers, No. 408; 1920.

fine sorbitic condition to a "divorced" or spheroidized pearlite as shown in Fig. 34. The magnetic properties of the corresponding specimens are given graphically in Figs. 35 and 36. Without discussing here the significance of the various properties revealed by the magnetic tests, it will be evident that the properties of the

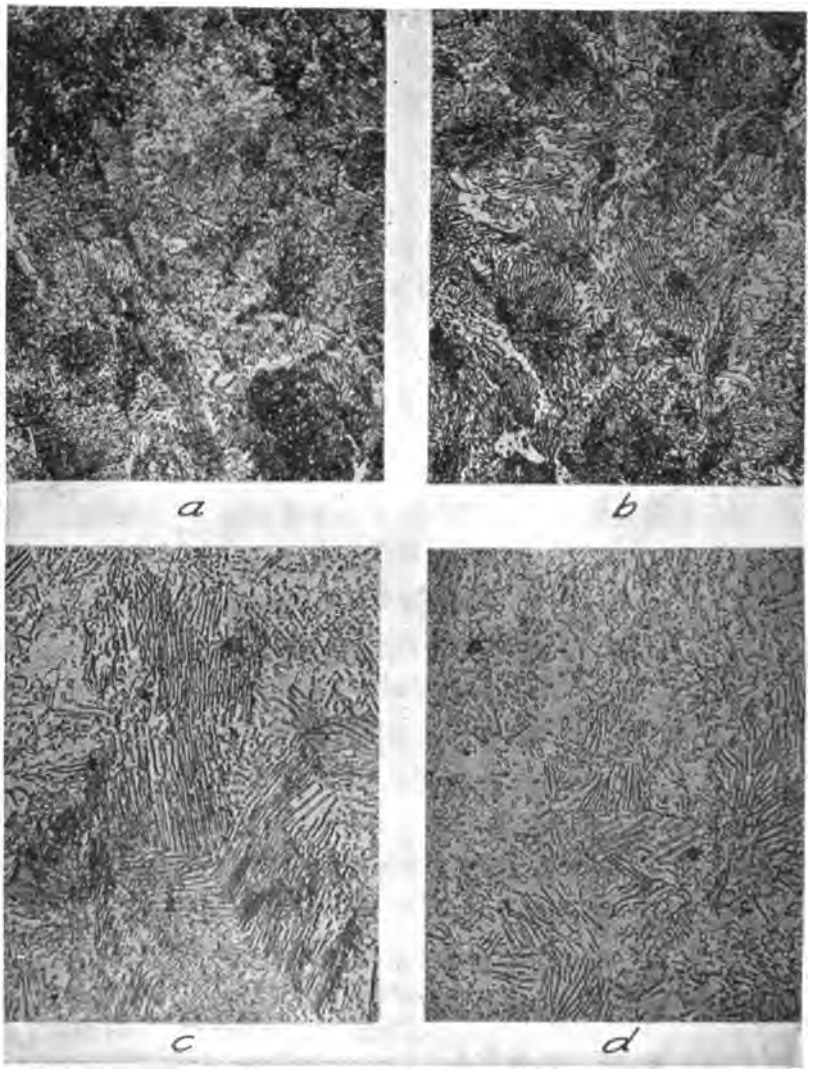


FIG. 34.—*Microstructure of eutectoid carbon steel (0.85 per cent carbon) showing the effect of rate of cooling upon the physical state of the pearlite.* × 500

Note how the lamellae constituting the pearlite became much thicker and more pronounced as the annealing progressed. The physical properties of the material also changed in corresponding manner. The specimens were heated to 800° C and cooled as follows: (*a*) Cooled in air, the material consists largely of sorbite; (*b*) cooled in lime, the material contains patches of fine lamellar pearlite and some sorbite; (*c*) cooled in furnace coarse lamellar pearlite with some spheroidizing of the pearlite has resulted; (*d*) cooled in furnace at a much slower rate than in *c*, the pearlite was largely spheriodized or "divorced." Etching reagent, 5 per cent alcoholic solution of picric acid

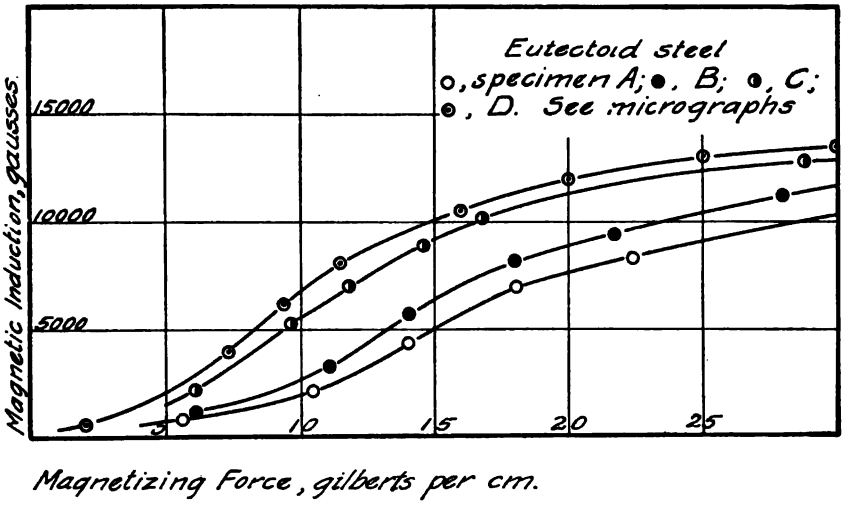


FIG. 35.—*Magnetic properties (induction vs. magnetizing force) of eutectoid carbon steel after different annealing treatments*

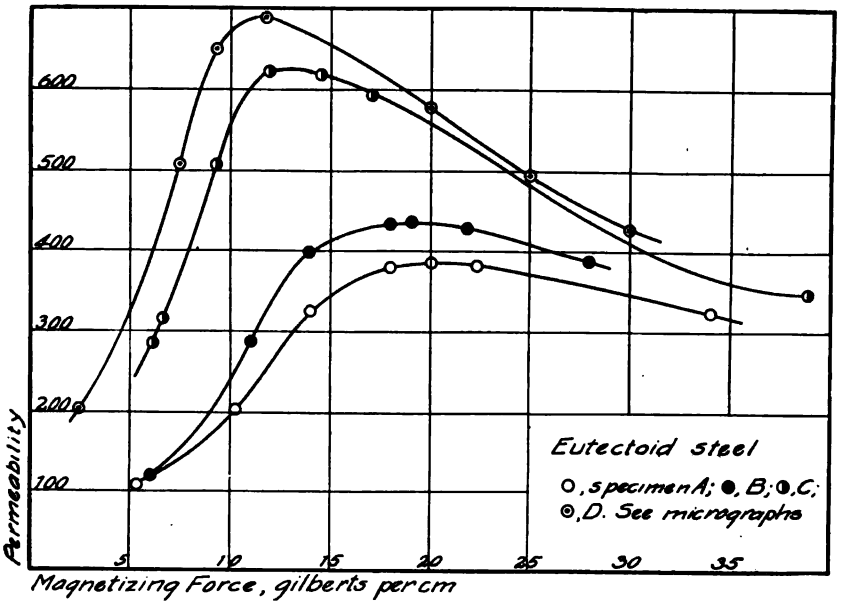


FIG. 36.—*Magnetic properties (permeability vs. magnetizing force) of eutectoid carbon steel after different annealing treatments, replotted from Fig. 35*

steel are affected to a marked degree by the changes which have been brought about in the physical state of the pearlite. Corresponding differences in the mechanical properties would also be found upon testing, although perhaps of not so great a magnitude as in the magnetic properties, since the magnetic tests are much

more sensitive than the ordinary mechanical ones and often reveal changes which are detectable by almost no other means.

2. CHEMICAL PROPERTIES

The chemical property of metals and alloys which is probably most important industrially is that designated by the rather loose term of "solubility." Upon this property depends the etching of metallographic specimens, the coloring of metallic surfaces, the corrodibility of materials under service conditions, and often, by

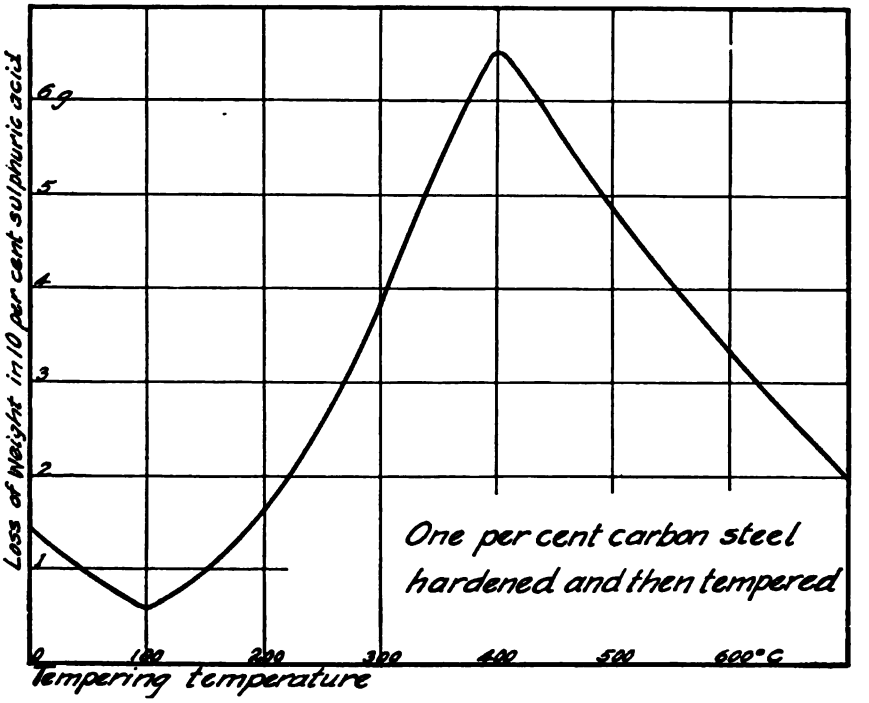


FIG. 37.—*Variation in the solubility of 1 per cent carbon steel in dilute sulphuric acid, after hardening and tempering to different temperatures.* (*Hanemann*)

the selective corrosion of certain constituents, the complete deterioration of the entire alloy in service. This property of an alloy is often influenced to a marked degree by the structure, and the following examples are cited as typical of this effect of structure upon properties.

(*a*) ETCHING

The etching of the polished surface for revealing the microstructure is dependent primarily upon the relative solubility of the constituents comprising the alloy. In case of a one-constituent alloy the difference in the rate of solubility of the various crystals,

which in turn results from the orientation of the sectioning plane relative to the inner structure of the different crystals comprising the alloy cut by this plane, is the fundamental reason for the production of the etch pattern. It is a well-established fact that the solubility of a crystalline material varies considerably when measured in different directions in one and the same crystal.

The constituents of binary as well as of more complex alloys practically always differ in their electrochemical properties, one being electropositive to the others. Consequently such a constituent will be attacked by an etching reagent in preference to the others, which remains bright and often stand out in slight relief above the surface. The microconstituents behave then very similarly to two dissimilar metals in contact with each other in an electrolyte, as is illustrated by steel coated with copper, nickel, or tin, which are all electronegative toward iron (or steel) and which thus accelerate the corrosion of the iron base of the coated sheet after it has been exposed by abrasion or in other ways. A zinc coating on the other hand being electropositive to iron, the two being in contact within an electrolyte, protects the exposed spot of iron for a considerable time at the expense of itself until the exposed area becomes too large.

FIG. 38.—*Appearance of a 1 per cent steel rod hardened, differentially tempered, and then immersed in dilute sulphuric acid.* × 1

The hardened rod was differentially tempered by heating the end x, the other one being kept cold by water. Note the narrow ring encircling the rod where the action of the acid upon the material was most intense

(*b*) SOLUBILITY OF TEMPERED STEELS

It is quite well recognized that the solubility of steel varies considerable according to the heat treatment which it has previously received. Fig. 37 illustrates this variation of solubility according to treatment.[21] A rod of high-carbon steel (approximately 1 per cent carbon) was hardened by quenching in water from a temperature of 765° C. The hardened rod was differentially tempered by heating one end to approximately 850° C while the other was kept cool with water. Thus the rod represents, at different points along its length, tempering to all temperatures

[21] H. Hanemann, Einfuhrung in die Metallographie and Wärmebehandlung, p. 87.

between the two extremes. When immersed in dilute sulphuric acid (20 per cent solution) for 17 hours the appearance shown in Fig. 38 was produced. The material in one of the intermediate stages of tempering is the most readily soluble, rather than the very hard or the very soft portions.

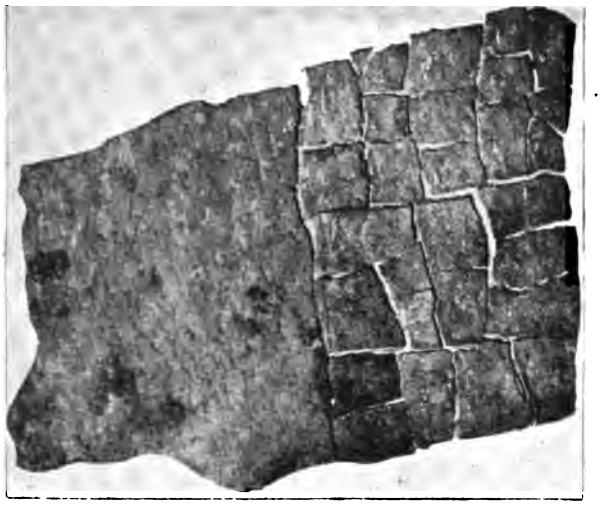
Considerable attention has been given to this property of tempered steels by foreign metallurgists, and it has been shown, as is illustrated by Fig. 37, that the rate of solubility can be used as an index of the tempering a specimen of steel has received. Maximum solubility corresponds to a tempering at 400° C. A special name, "osmondite," has been given to steel in this particular condition, on account of its characteristic properties.

From Figs. 37 and 38 it is evident that the rate of solution is profoundly affected by the structure of the steel. In the form of the solid solution the material is the least soluble. As the degree of tempering is increased and the carbide held in solid solution is progressively precipitated, the rate progressively increases. The maximum solubility occurs in the troostitic steel after the simple solid solution has been changed by tempering into a state of agglomeration resembling that of an emulsion. The material in this condition is not resolvable under the microscope into its constituent parts. As the tempering is continued, progressively higher temperatures being used, the ultramicroscopic particles increase in size until finally the ordinary microscopic examination reveals them. This increase in the size of particles of the constituents is accompanied by a decreased solubility, although the fully annealed specimen is somewhat more soluble than is the material in its initial or fully hardened state.

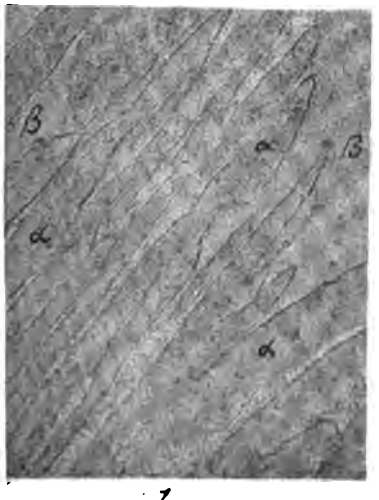
(c) CORROSION

This term when strictly used refers to the tendency of metals to revert to the stable form in which they occur in nature; that is, the oxide. The subject is so broad and the contributing causes so many and so varied that considerable differences of opinion are held as to the mechanism by which the process of corrosion is brought about. Only a brief mention will be made here of how structural features may aid in the process.

In general, the corrosive attack of a metal is more pronounced in the direction of the "fibers" than across them. This is most marked in case of accelerated corrosion by exposure to sea air, sea water, or similar conditions, and is found in all types of readily corrodible alloys if in the wrought state. This may be attributed



a



b

c

FIG. 39.—*Appearance of a corroded brass sheet together with the microstructure of the unchanged and of the corroded metal*

Note how brittle the sheet *a* was after corrosion. This was the result of a selective corrosive attack of one of the two microconstituents which make up the alloy. (*a*) The brass sheet, approximate composition, copper, 60 per cent; zinc, 40 per cent, became so brittle after corrosion in sea water that it could be broken into fragments with the fingers as shown. × 1. (*b*) Microstructure of Muntz metal showing the two constituents α and β. × 500. Etched with ammonium hydroxide and hydrogen peroxide. (*c*) Microstructure of a corroded sheet of Muntz metal after 7 years exposure in sea water; the β constituent disintegrated into a weak pulverulent material resembling copper. × 500. The specimen was etched with ammonium hydroxide and oxidized in the air

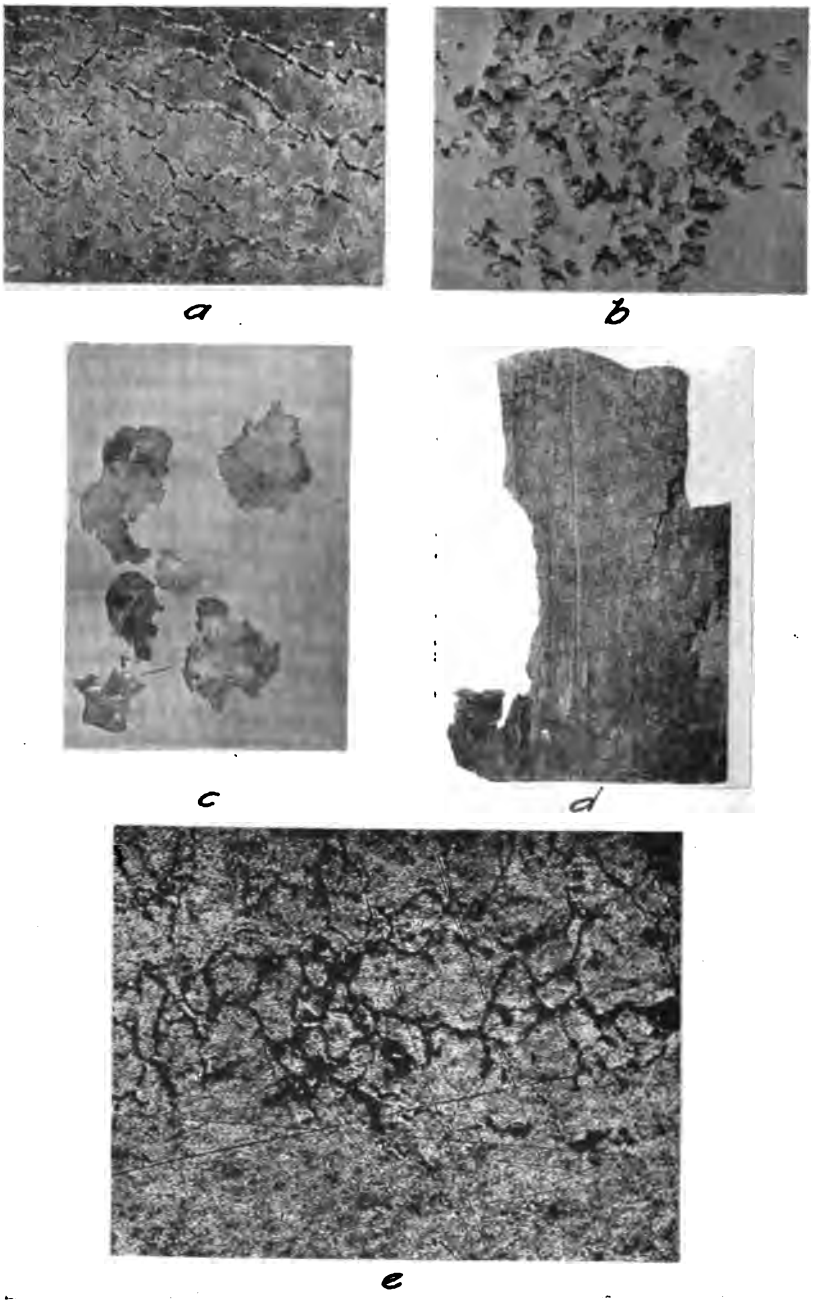


FIG. 40.—*Appearance of lead after accelerated corrosion and of commercial lead which corroded in service*

Note in *e* how the bond between the crystals of lead may be so weakened under certain conditions as to permit the metal to be crumbled as shown in *b*. (*a*) Surface appearance of a sheet of high-grade lead (99.99 per cent) after immersion of 24 days in a solution of lead acetate (N) and nitric acid (0.8 N) and bent at a slight angle. An intercrystalline brittleness resulted from the corrosive attack; × 5. (*b*) Crystals which were detached from a sheet of commercial lead (lead, 99.72 per cent; antimony, 0.07 per cent; iron, 0.02 per cent; tin, 0.14 per cent) immersed for 4 days in an acidified solution of lead acetate (400 g lead acetate, 100 cm^3 nitric acid, 1000 cm^3 water). × 8. The corrosion of the lead was intercrystalline in nature. (*c*) Some of the crystals of *b* flattened out. × 8. Each crystal retained the characteristic malleability of lead, although the sheet as a whole was brittle. (*d*) Appearance of a lead cable sheathing which corroded in service, approximate composition: tin, 1.09 per cent; lead 98.3 per cent. × 1½. (*e*) Cross section of specimen *d*, unetched. The upper edge of the micrograph coincided with the outer surface of the sheath. The corrosive attack of the metal was intercrystalline in its nature. × 50

largely to the mechanical effect of inclusion streaks by affording lodgment for moisture, so that the attack at such points is accelerated and access to the interior more readily gained along the line of the inclusion. Similar instances have been noted in wrought-aluminum alloys, in which it appears that the difference in the electrochemical properties of streaks of the metal in various stages of cold working is responsible in a large degree for the fibrous appearance of the corroded ends of wrought rods.

Brass of the type termed Muntz metal, approximately 60 per cent copper and 40 per cent zinc, exemplifies well the specific effect of a metallographic constituent upon the corrosion of a metallic material. Such a brass has a duplex structure as is shown in Fig. 39 *b*, one constituent, the α, being much richer in copper than is the second, or β. The zinc-rich constituent is quite readily attacked by sea water, the difference in the electrochemical potential of the two, α and β, contributing to bring about the difference in the resistance of the two to the action of the electrolyte. The zinc from the β is leached out, and a spongy mass resembling copper remains, filling the spaces previously occupied by the β (Fig. 39 *c*). Thus the alloy is converted into a weak brittle mass consisting of a sponge of the more or less attacked α constituent and the pulverulent material resulting from the disintegration of the β. Material of this kind in the form of sheets often becomes so brittle that it can be readily broken into small fragments in the fingers (Fig. 39 *a*).

A soft ductile metal like lead may under some conditions of accelerated corrosion become so brittle that it can be crumbled to powder in the fingers. This is most apt to occur if the lead is somewhat impure. Fig. 40 shows a section of a lead cable sheath which by electrolytic corrosion became so brittle that it could be reduced to a granular powder. Each grain, however, retained its initial ductility and other characteristic properties of lead. The corrosive attack of the metal was essentially intercrystalline in character (Fig. 40 *d*) which was, in all probability, due largely to the impurity contained by the metal (1.09 per cent tin), although it has been shown [22] that lead of exceptionably high purity (99.99 per cent) is subject to intercrystalline brittleness under certain conditions. In the corroded lead illustrated in Fig. 40 most of the impurities which are present exist as

[22] H. S. Rawdon, Intercrystalline Brittleness of Lead, B. S. Sci. Papers, No. 377; 1920.

tiny lodgments, sometimes as a eutectic, between the crystals of lead; thus the corrosive attack is localized to a large extent, and the metal as a whole shows intercrystalline brittleness.

(*d*) VARIATION IN COMPOSITION THROUGHOUT AN ALLOY

In some alloys the composition varies at times to such an extent throughout the body of the alloy that the properties, both chemical and physical, are far from being uniform for the material. Examples of this have already been spoken of (Sec. III, 2). Segregation, as in steel, caused by the selective process of freezing, is responsible for many such marked cases of chemical unhomogeneity. Fig. 41 illustrates a marked case of such unhomogeneity in lead-antimony alloys because of the difference of density of the constituents of the alloy, the cause in this case being usually spoken of as "liquation." It is evident without further discussion that a specimen cut from the lower portion of each of the ingots will show properties which will differ markedly from those of a specimen taken from near the top of the ingot.

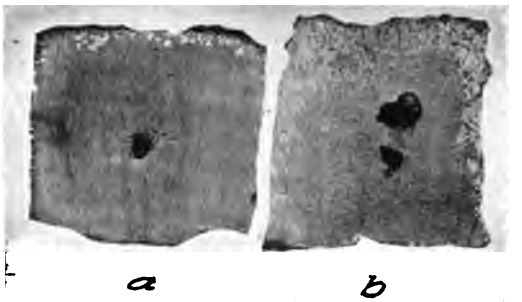


FIG. 41.—*Chemical unhomogeneity of lead-antimony alloys caused by "liquation" during slow cooling.* × 1

Note the layer of the white constituent in each specimen. This consists of antimony crystals which collected at the top of the ingot during solidification. This illustrates one of the difficulties encountered in preparing bearing metal alloys. (*a*) Lead-antimony alloy containing approximately 15 per cent antimony. The greater part of the small ingot is composed of the eutectic which contains 13 per cent antimony, the excess antimony rose to the top of the molten metal because of its lower density. (*b*) Similar alloy containing 22 per cent antimony. The specimens were etched with dilute hydrochloric acid and then slightly repolished

VI. APPLICATIONS OF THE MICROSCOPY OF METALS

The most important industrial application of the microscopy of metals is undoubtedly its use in connection with the heat-treatment of steels. Not only is it used extensively as a routine method of examination of heat-treated stock to make certain that the prescribed treatment has been carried out and also to show wherein lies the fault when the material after treatment does not have the expected mechanical properties, but it is of

inestimable service in specifying a proper heat treatment for new types of steels. A second important application of the method is as a supplement to chemical analysis. It is believed, however, that the description of the various applications can best be given by means of short references to a few typical cases chosen from numerous materials examined at the Bureau of Standards than by a longer and more general discussion such as exists already in some of the textbooks on the subject of metallography.

1. RELATION TO HEAT TREATMENT

As has been previously stated (Sec. V, 1, *d*) the grain size of a metal is of very considerable importance in affecting the properties of the material. In most cases the microscope should be depended upon for revealing accurately the relative grain size of metallic materials, although considerable information can be gained by examining the fracture of broken test specimens, and it is claimed by some that for some materials, particularly alloy steels, the examination of the fracture is the only sure way of arriving at this information. If a numerical expression of the grain size is desired, the method recommended by the American Society for Testing Materials may be used.[28]

Fig. 22 shows a medium-carbon steel (carbon 0.46 per cent) which has been "overheated"—it was maintained for six hours at 1110° C. The steel was not permanently injured, however, and it was "restored" by proper annealing as shown in Fig. 22 *c*. However, material which is heated at so high a temperature that it is properly described as "burnt" is useless; it can not be restored and made safe for use by any treatment now known short of remelting. The heating of steel to the temperature at which incipient fusion on the surface occurs does not, however, always necessarily entail "burning" of the material. For some of the special alloy steels used for high-speed cutting purposes, the heat treatment recommended usually includes "heating to incipient fusion." The restoration of the material after overheating depends upon the phase change which occurs in the alloy at its critical temperature. Such a simple means for removing the structural effects of overheating could not be applied to a metal such as copper, for example, which exhibits no phase changes upon heating.

[28] Proc. Am. Soc. for Testing Materials, Specifications E 2–20, Micrographs of Metals and Alloys, Part 1; 1920.

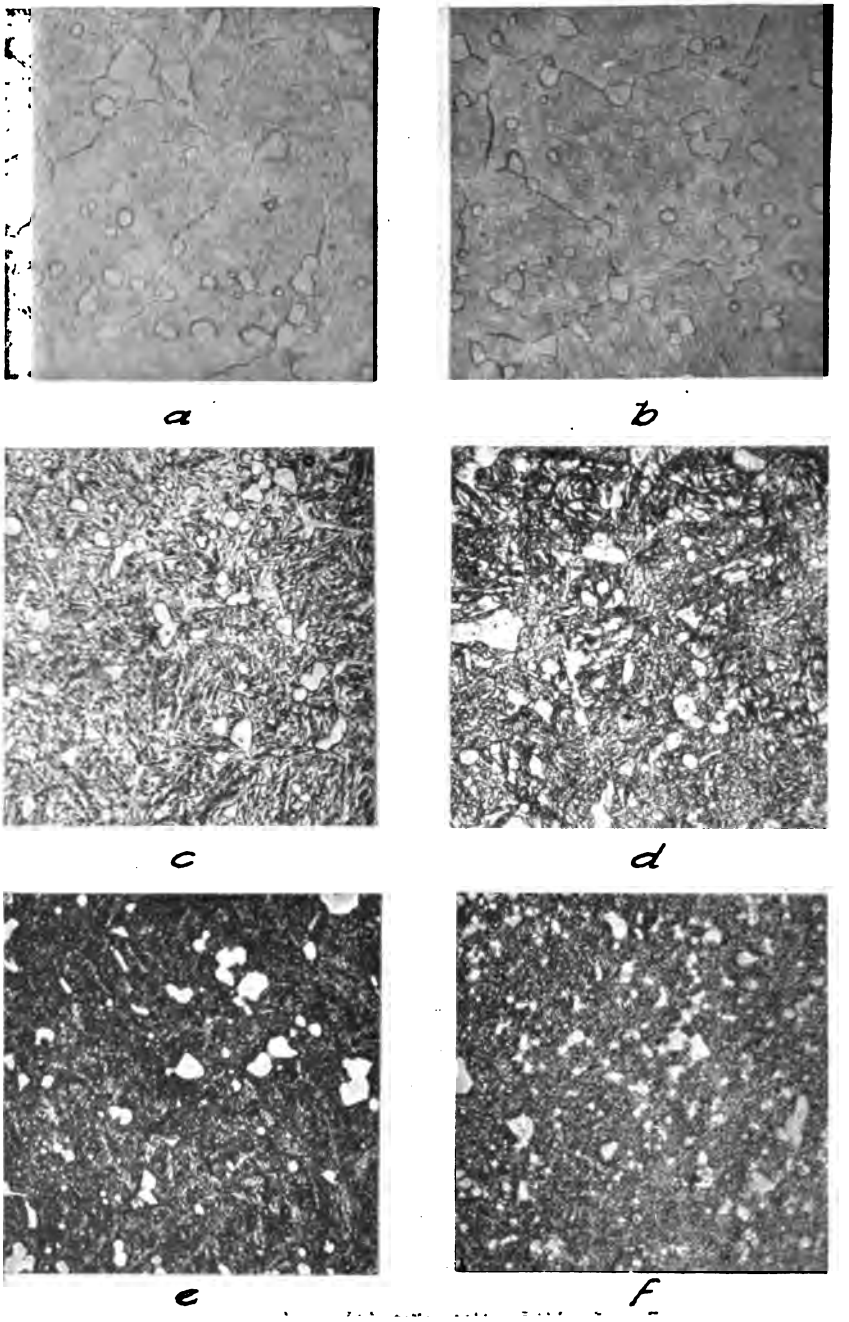


FIG. 42.—*Microstructure of high-speed tool steel illustrating the effect upon structure of tempering the hardened steel at different temperatures.* × 500

The micrographs show the structure of a steel containing 0.77 per cent carbon, 17.8 per cent tungsten, 3.5 per cent chromium, and 0.74 per cent vanadium after the treatments given below: (*a*) Quenched in oil from 1290° C. A polyhedral structure resulted from this treatment and the material was rendered largely austenitic in its properties. (*b*) Specimen *a*, tempered 30 minutes at 200° C. The crystals show interior markings suggestive of the beginning of the change into the martensitic condition. (*c*) Specimen *b*, tempered 30 minutes at 400° C; the martensitic pattern has been fully developed. (*d*) Specimen *c*, tempered 30 minutes at 600° C; although in the troostitic state, the martensitic pattern is still evident. (*e*) Specimen *d*, tempered 30 minutes at 700° C. Tiny globules of compound of tungsten precipitated from the previously existing solid solution by the process of tempering have begun to appear. (*f*) Specimen *e*, tempered 30 minutes at 800° C. The particles are more plainly visible than in *e* and the material is approaching the annealed state. Etching reagent, 2 per cent alcoholic nitric acid

A knowledge of the microstructure is very helpful in explaining the peculiar characteristic properties of high-speed tool steels in order to specify properly the necessary heat treatment.[24] When quenched from a sufficiently high temperature the material is, at least partially, austenitic in structure. Upon tempering at a relatively low temperature, it is converted into the martensitic state, with an accompanying gain in hardness, usually termed secondary hardness. The martensitic state is changed into the troostitic condition only very slowly, so that the material passes no further than the troostitic state upon tempering at a relatively high temperature. Hence this state, together with the accompanying cutting properties (toughness and hardness), is retained by the material at the high temperature which prevails in the use of such tools. Fig. 42 illustrates some of the characteristic structural features of tempered high-speed steel.

High-carbon steels maintained for a considerable time at the "annealing temperature" will sometimes show evidence in their structure of the formation of graphite at the expense of the cementite. Such a steel is, of course, useless for most purposes and particularly so for the purposes for which high-carbon or tool steel is commonly used. Fig. 21 shows the structure of a tool steel (approximately 1 per cent carbon) which was spoiled in this manner.

Fig. 43 shows the structures which may be obtained by hardening a hypoeutectoid steel (carbon, 0.46 per cent) by quenching from different temperatures. When a temperature only slightly above the A_1 transformation is used, considerable ferrite exists intermixed with the martensite, and the material has not been fully hardened. When quenched from above the A_{2-3} transformation temperature, no ferrite remains, and a fine martensitic structure results. If a still higher temperature is used, the structure becomes very coarse, and intercrystalline cracks often form upon quenching. The time interval for which the material is maintained at the temperature before quenching must, of course, be taken into consideration in work of this kind.

Fig. 44 shows the structure of a steel cylinder, used as a container for compressed gas, which exploded during use. The specifications for this material required that the steel be tempered after hardening, the desired structure being shown in Fig. 44 *b*. It is evident from the fact that the structure of the defective

[24] H. Scott, Relation of the High-Temperature Treatment of High-Speed Steel to Secondary Hardening and Red Hardness, B. S. Sci. Papers, No. 395; 1920.

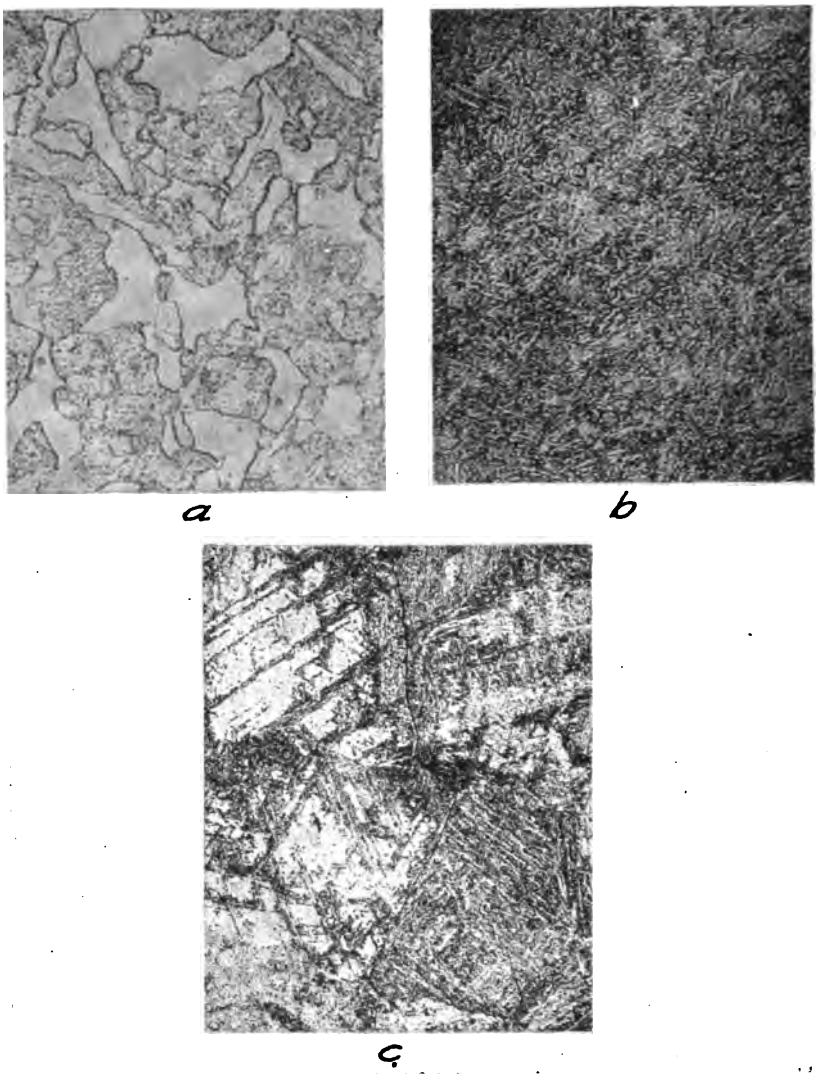


FIG. 43.—*Microstructure of medium carbon steel after different hardening treatments*

Note the light colored constituent in *a*. This indicates that the steel was not fully hardened by the treatment given. The large crystals in *c*, together with the fine quenching cracks, show that the hardened treatment was too severe. (*a*) Specimen of 0.46 carbon steel quenched in water after heating 15 minutes at 750° C (1380° F), just above the A_1 transformation. The structure consists of ferrite and martensite. × 500. (*b*) Specimen similar to *a*, quenched in water after heating 15 minutes at 850° C (1515° F), just above the A_3 transformation. The structure consists entirely of very fine martensite. × 500. (*c*) Specimen similar to *a*, quenched in water after heating 15 minutes at 1200° C (2190° F). A very coarsely grained martensitic structure has resulted, in which intercrystalline quenching cracks are abundant. × 100. Etching medium, 2 per cent alcoholic solution of nitric acid

cylinder (at least at the end where failure occurred) was comprised of martensite and troostite, that the tempering operation for this particular cylinder was omitted through some oversight, and that the subsequent failure of the material resulted from faulty heat treatment, although the cylinder successfully withstood the required hydraulic-pressure test.

Undesirable properties of steel are sometimes attributed to faulty heat treatment used for the material, a microscopic examination of which shows that the cause is an entirely different one. A section of a forging of nickel steel intended for rifle parts was

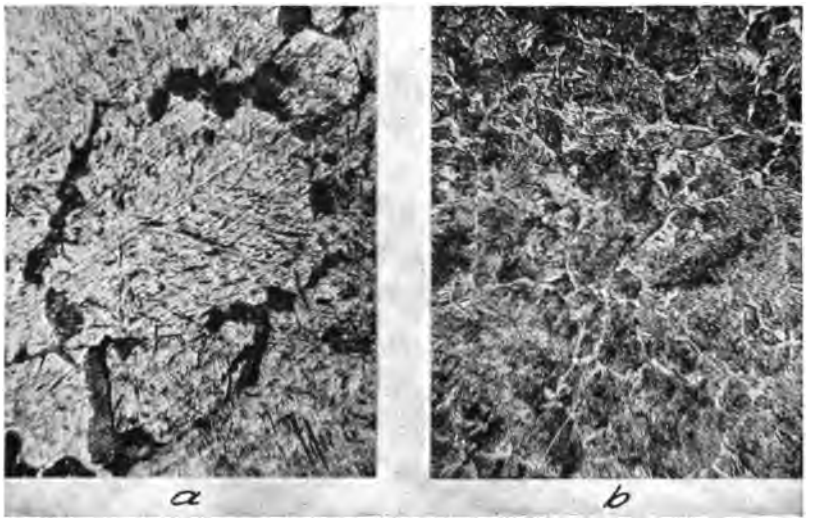


FIG. 44.—*Microstructure of a heat-treated steel container for compressed gas which failed in service.* × 250

(*a*) Structure of one of the fragments from near the point at which the explosion occurred; the material consists of martensite and troostite. Etching reagent, 1 per cent alcoholic solution of hydrochloric acid. (*b*) Structure of a specimen of steel similar to *a*, showing the microstructure desired and which should have resulted from the specified treatment. Etching reagent, 2 per cent alcoholic solution of nitric acid. It is evident that the explosion of the cylinder was the result of a lack of tempering of the hardened material

submitted for examination. Difficulties had been encountered in drilling, and the attempt made to overcome these by various annealings of the material. The microscopic examination of the annealed piece revealed a martensitic core, while the outer portions were of the usual ferrite-pearlite structure (Fig. 45). Subsequent chemical analysis showed that the nickel content of the central portion was very much higher than that of the outer parts, enough so as to render the material martensitic even upon slow cooling. Evidently heat treatment could not be expected to improve the machining properties of such material; the remedy had to be sought in the melting practice used in the production of the steel.

An interesting example of a defect which may result in copper which has been improperly annealed, is shown in Fig. 46. The metal was rendered brittle and useless by numerous fine intercrystalline cracks throughout the interior. This is to be attrib-

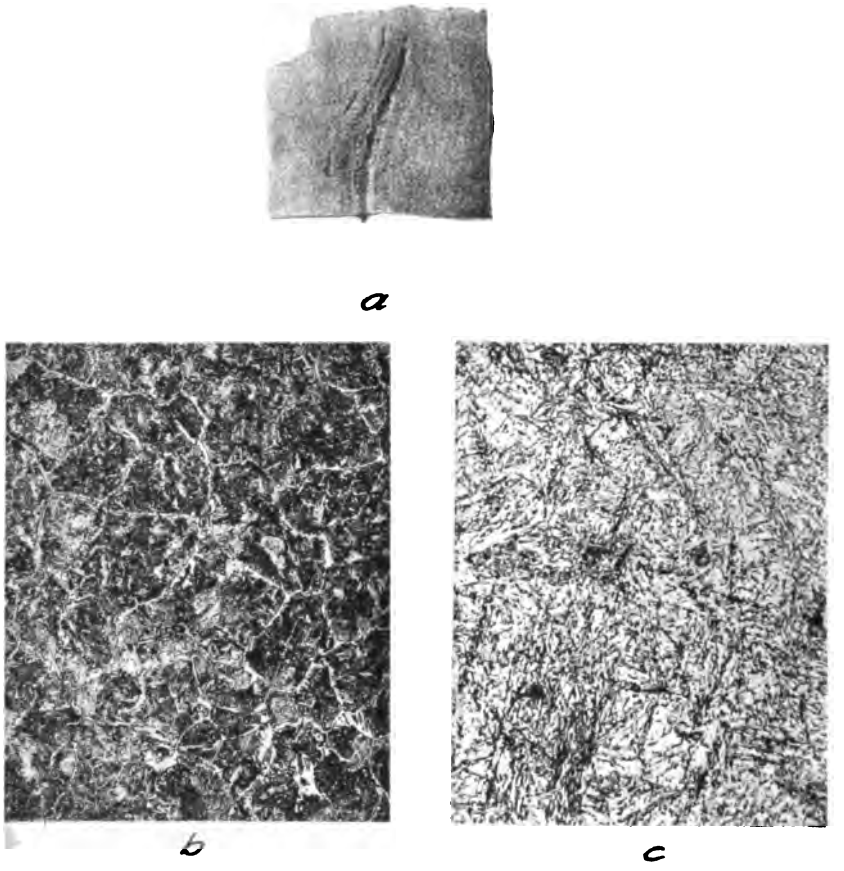


FIG. 45.—*Structure of a defective nickel steel forging caused by improper melting practice*

Note the dark central streak in *a*. This was of a martensitic structure, *c*, and rendered the material too hard to machine properly. This defect could not be remedied by heat treatment. (*a*) Macrostructure of a longitudinal section deeply etched with concentrated hydrochloric acid, showing the core caused by the nondiffusion of nickel in the molten steel. × 1. (*b*) Microstructure of specimen *a*, as received from the mill, outside the core. × 100. (*c*) Microstructure of the core of specimen *a*, as received from the mill. The nickel content of this part was so high that it remained martensitic even upon slow cooling. × 500. Etching reagent, *b* and *c*, 2 per cent alcoholic solution of nitric acid

uted to the action of the atmosphere in which it was heated rather than to the temperature used. The particles of cuprous oxide, which are always present to some extent in remelted copper, are reduced by hydrogen or other reducing gases which readily pene-

trate the heated metal. The pressure of the gaseous products resulting from their action upon the oxide is sufficient to produce the internal cracks throughout the hot metal.

2. SUPPLEMENT TO CHEMICAL ANALYSIS

Several instances have already been given to show how a knowledge of the structure of an alloy may be a very valuable aid in sampling the material for chemical analysis. This is particularly true for segregated alloys (Figs 2 and 16) and for those in which liquation readily occurs (Fig. 41).

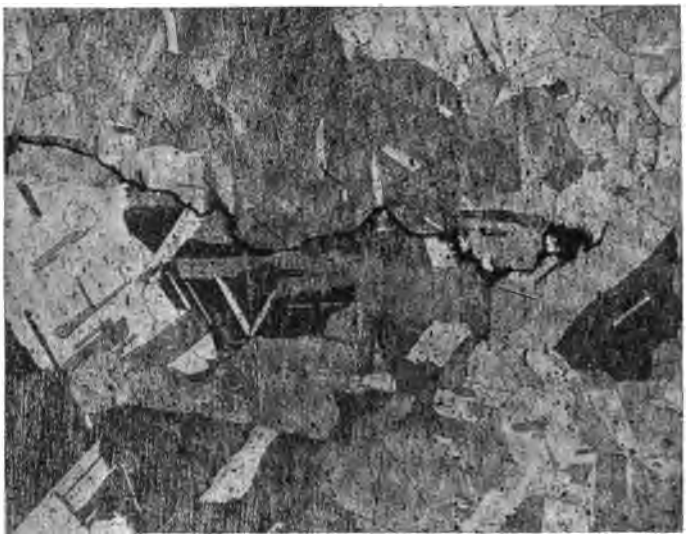


FIG. 46.—*Microstructure of copper which was spoiled in annealing as a result of the nature of the surrounding atmosphere.* × 100

Note the fine intercrystalline cracks which formed in the interior of the metal. Such material is commonly termed "gassed" copper. Etching reagent, ammonium hydroxide and hydrogen peroxide

The microscopic method is of decided value in supplementing the chemical study of the various metallic coatings used for protective purposes, particularly on iron and steels. In Fig. 47 the complex structure of a "brass" coating is shown. The coating in reality consists of three layers, one of nickel and two of brass. It is evident that with this information in mind, the chemical determination of this coating can be carried out and interpreted in a much more logical way than without it. Fig. 47 *b* shows the duplex structure of electrolytic deposit of alternate layers of copper and nickel. The microscopic method may be used also in determining the thickness and distribution of the coating

material; although laborious, this method is often the only one available for such determination. Fig. 48 illustrates an application of this.

By means of microscopic studies of the constituents comprising the coating of tinned copper, an explanation has been found for the corrosion pitting of copper roofing which had been treated with a "protective" coating of tin, Fig. 49.[25] One of the constituents

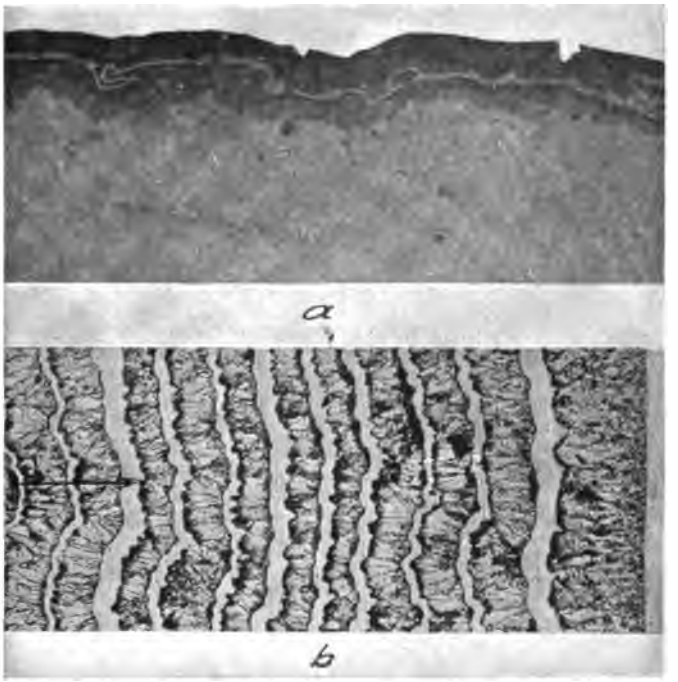


FIG. 47.—*Microstructure of complex metallic coatings produced by electrolytic deposition*

(*a*) Cross section of a "brass" coating used on a steel base; the coating consists of three layers, the intermediate one being of nickel (× 500); (*b*) cross section of an electrolytic deposit consisting of alternate layers of nickel (light) and copper (crystalline), the metal being deposited in the direction shown by the arrow (× 100). Etching reagent, ammonium hydroxide and hydrogen peroxide

formed by the interaction of tin and copper is electronegative to copper, the two being in contact within an electrolyte, and thus it stimulates the corrosive attack upon the latter when the two are exposed simultaneously to corroding influences. Other applications of the use of the metallographic microscope to the study of metallic coatings have been discribed in a previous publication.[26]

[25] P. D. Merica, B. S. Tech. Papers, No. 90.

[26] B. S. Circular No. 80, Protective Metallic Coatings for the Rustproofing of Iron and Steel.

Because of the relatively higher price for wrought iron as compared with mild steel there is at times a tendency to "adulterate" this product with additions of the cheaper metals. While the chemical analysis will indicate in a general way when such additions have been made, the metallographic method is almost indispensable for quickly revealing the extent of such contaminations. Fig. 50 shows the appearance of a specimen of commercial wrought iron which has been suitably prepared to show the results produced by the addition of low-carbon steel to material of this kind.

Considerable importance is attached to the study of the occurrence of gases in metals, and in particular those gases which are given off by steel when heated in vacuo. Among the principal

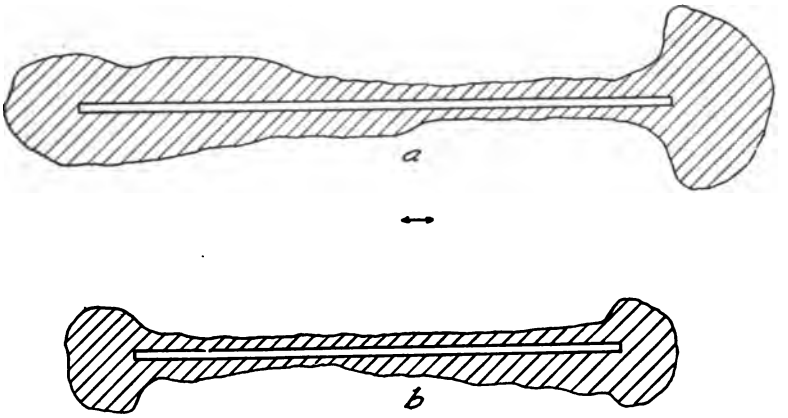


FIG. 48.—*Variation in thickness of an electrolytic zinc coating such as may occur on flat sheets after plating, determined by microscopic measurements*

The shaded portion represents the coating drawn to the scale indicated by the arrow, the length of which represents 0.094 mm. The cross sections of the plate upon which the coating was deposited are shown somewhat less than natural size, the longer one was a diagonal section of a 4-inch square plate, the shorter one was a parallel section ½ inch away

gases obtained in this manner is carbon monoxide. A study of the microstructure of specimens of steel after being heated in vacuo [27] shows that an appreciable decarburization occurs in such material, which fact throws considerable light on the origin of at least some of the evolved gases. Fig. 51 shows the condition existing at the surface of a specimen of low-carbon steel (0.18 per cent carbon) after heating in vacuo above the transformation temperature. The carbon was removed for a considerable depth at the surface. Evidently a chemical reaction, the reverse of that by which carburization of steel in the cementation

[27] H. S. Rawdon and H. Scott, Microstructure of Iron and Mild Steel at High Temperatures, B. S. Sci. Papers, No. 356.

or casehardening process is brought about, occurred during the heating. In the usual process of carburization, carbon penetrates the metal as carbon monoxide, which later reacts with the iron to form iron carbide (cementite) and carbon dioxide, which diffuses outward from the metal. In the decarburization of steel in vacuo the carbon evidently leaves the metal as a gas; this would necessitate the presence in the material of oxygen in some form which, by a reaction with the carbide, forms the gas which is later removed by the action of the vacuum pump. Steels made under

FIG. 49.—*Appearance of the exposed surface of corroded tinned copper sheating used for roofing purposes.* × 1

Note the corrosion pits which occurred in service, some of which penetrated through the sheet. These were the result, in large measure, of the tin coating which was applied to the copper

widely varying conditions differ markedly in the amount of decarburization which occurs, as is to be expected, according to the amount of oxygen retained by the metal. The material shown in Fig. 51 was a laboratory specimen made by the addition of carbon to pure iron, no further additions being made for deoxidation or other purposes. Hence it might be expected that such material would decarburize much more rapidly when heated in vacuo than a steel which had been thoroughly deoxidized by the proper additions to the molten metal.

The chemical determination of "slag" in steel is, at its best, rather unsatisfactory. Even if good checks are obtained in dupli-

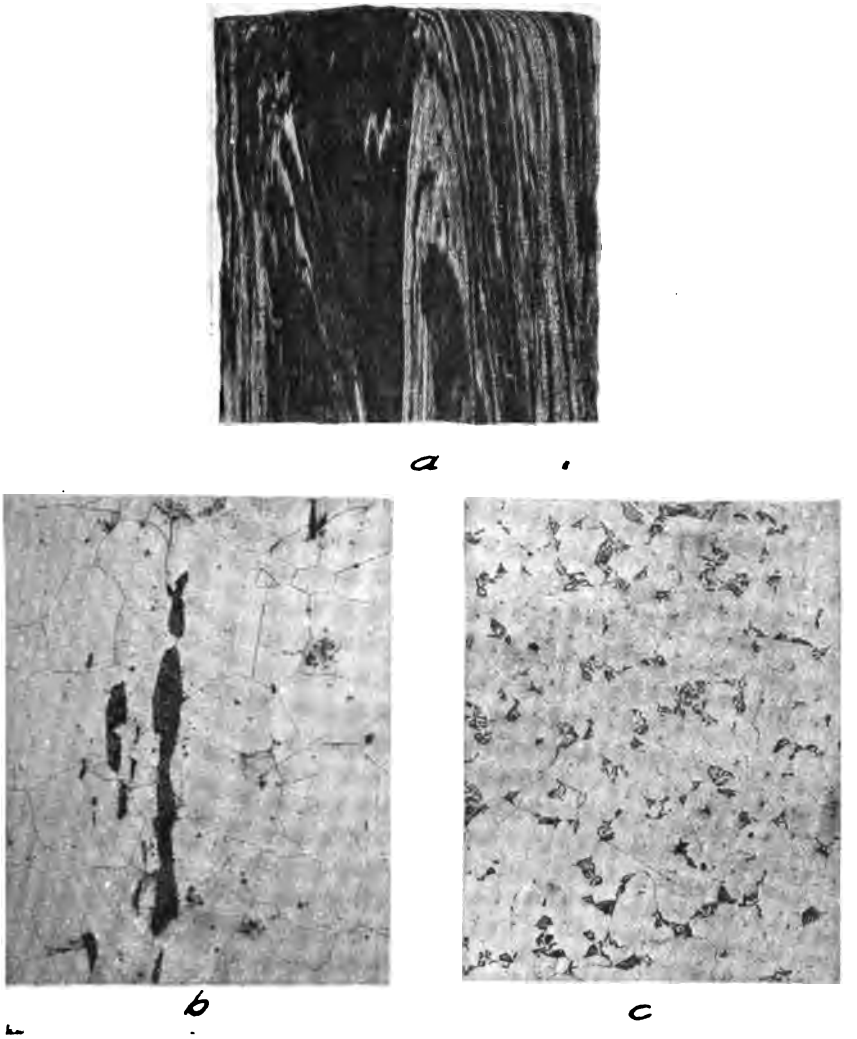


FIG. 50.—*Structure of wrought iron to which additions of steel have been made*

Note the white streaks *a*. Such an appearance after suitable etching is indicative of the addition of steel to wrought iron. (*a*) Macrostructure of a longitudinal section of a 2-inch round of wrought iron, deeply etched with hot concentrated hydrochloric acid. × 1. The white streaks represent the additions of steel. (*b*) Microstructure of the metal of dark portions of *a*. This has the characteristic structure of wrought iron. × 100. (*c*) Microstructure of metal of one of the light streaks of *a*. The metal is low-carbon steel. × 100 Etching reagent, 2 per cent alcoholic solution of nitric acid

cate determinations, the interpretation of the results is a matter of considerable difficulty. That this must be so is evident from Fig.

52, which shows the structure of a slag thread from wrought iron. The duplex nature of this simple slag is plainly shown, and it is evident in the case of the complex steels, in the manufacture of which the additions to the metal are often several in number and varied in composition, that the resulting "slag" must be correspondingly complex in its nature.

An illustration has already been given (Sec. IV, 1; Fig. 15) suggesting how it is possible to estimate rather closely the percentage composition of certain alloys with respect to certain elements from the structural appearance of the material alone, if the alloy is in the condition of stable equilibrium. This method is of

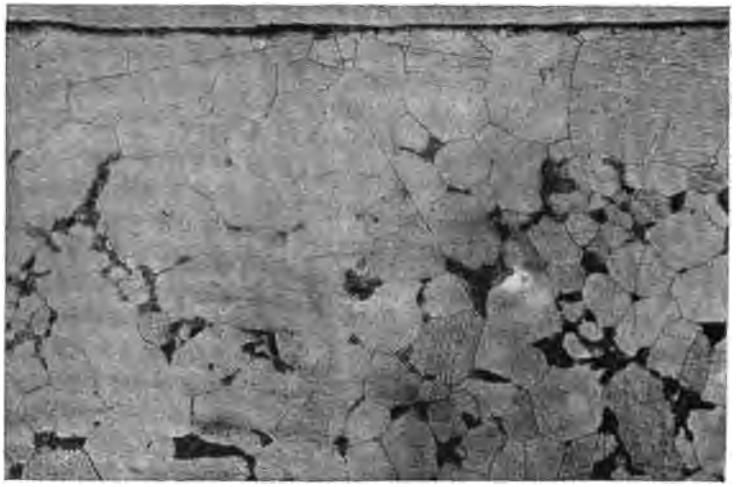


FIG. 51.—*Microstructure of an iron-carbon alloy which was decarburized by heating in vacuo.* × *100*

Note the absence of the black constituent (the carbon-bearing portions) for a considerable distance below the surface. The specimen (0.18 per cent carbon) was heated for 30 minutes at 760° C, and cooled in vacuo. The cross section shows the distance from the surface to which the carbon has been removed; etching reagent, 2 per cent alcoholic solution of nitric acid

importance from a practical standpoint in the estimation of oxygen in copper, a determination which, if carried out by chemical means, is very tedious and time consuming. Oxygen in copper exists in the form of cuprous oxide, which is soluble in the molten metal and upon cooling separates as the copper-copper oxide eutectic (Fig. 57) (3.45 per cent cuprous oxide; melting point, 1063° C.) in a manner exactly similar to certain metals, for example, silver and copper. From an estimation of the relative amount of the eutectic in cast copper, a rather close value of the percentage of oxygen present can be computed from the microstructure. Nickel is similar to copper in the formation of an oxide eutectic.

The microscope is often an indispensable means for determining the rôle played by certain additions made to alloys in the course of their preparation. This is true particularly for steels. Thus an examination of the structure of titanium-treated steels shows that this element, titanium, in the quantities usually

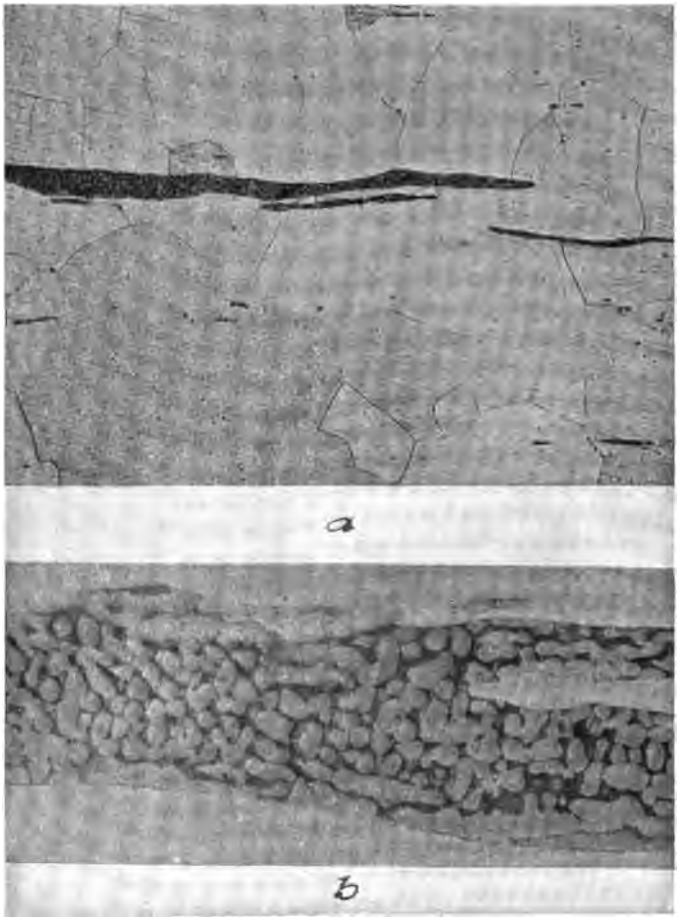


FIG. 52.—*Microstructure of wrought iron showing the complex nature of the slag*

(*a*) Longitudinal section of wrought iron showing a slag streak embedded in the ferrite crystals; etching reagent, 2 per cent alcoholic solution of nitric acid. × 100. (*b*) Slag streak similar to the one shown in *a*, unetched × 500. The duplex nature of the slag is very evident

added to steel, does not alloy with the metal in the sense that many added elements do. Its rôle is to free the metal of undesirable substances present and then leave the metal in the slag, carrying the detrimental substance combined with it. It appears to be especially active in combining with nitrogen,

Fig. 17 shows one of the characteristic inclusions found in steel which has been treated with titanium. Zirconium appears to act in a manner similar to that of titanium when added to steel in small amounts, in that it frees the metal from some undesirable substance (not necessarily nitrogen) and then escapes from the metal in some combined form in the slag. The inclusions which are found in zirconium-treated steel are of a very characteristic shape and yellow color (Fig. 53). On the other hand, the primary rôle of other added elements is to react with the steel and to modify the properties, either of the ferrite as in the case of nickel, or of the carbide as in the case of chromium.

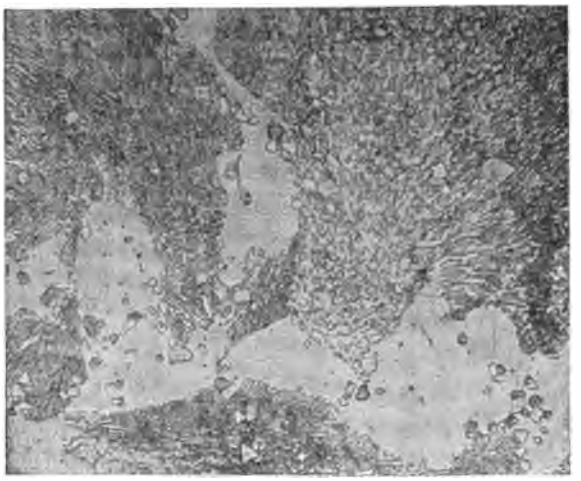


FIG. 53.—*Microstructure of steel to which additions of zirconium have been made.* × 500

The small light-colored inclusions, square or triangular in outline, are characteristic of steel to which zirconium has been added. They are of a striking lemon-yellow color. Etching reagent, 2 per cent alcoholic solution of nitric acid

The form in which certain elements occur in steel and their distribution throughout the metal are often of much more importance, as far as the properties of the metal are concerned, than the percentage of the element present. This has already been pointed out in the case of sulphur (Sec. IV, 1). Phosphorus in the amount usually present in iron and steel exists in solid solution in the ferrite. The distribution is often far from uniform throughout the metal (Fig. 5), and even within the individual crystals the distribution may be far from uniform, as is shown in Fig. 54.

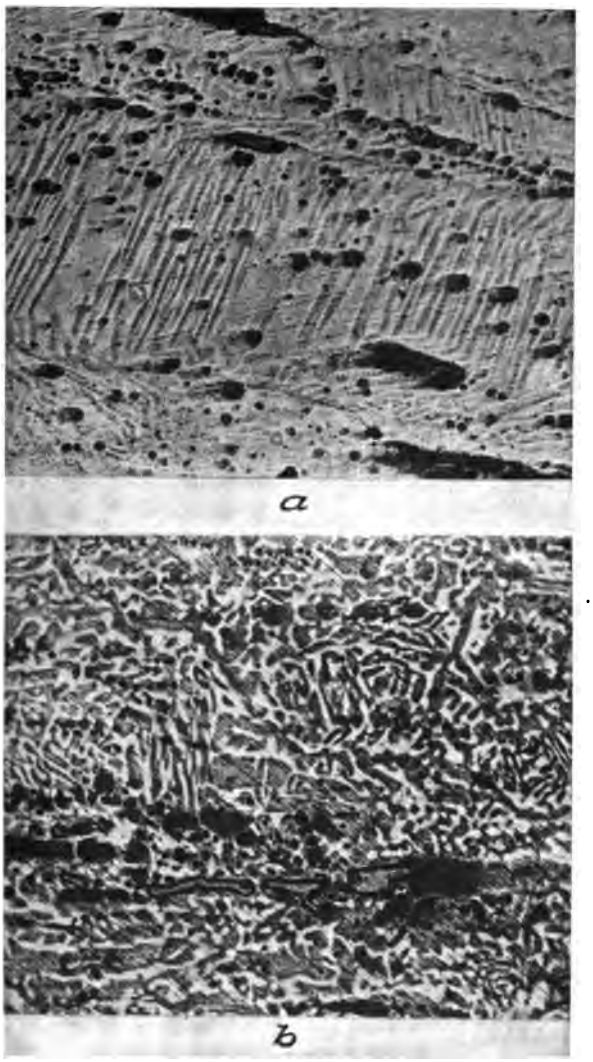


FIG. 54.—*Microstructure of wrought iron of high phosphorus content, showing the lack of uniform distribution of this element even within the individual crystals.* × 100

The parallel bands within the crystals, *a*, are indicative of very brittle iron. (*a*) Longitudinal section of wrought iron, high in phosphorus (0.36 per cent), annealed at 600° C. The phosphorus banding within the individual grains persisted after this treatment: etching reagent, 10 per cent alcoholic solution of nitric acid. (*b*) Longitudinal section of high phosphorus wrought iron, etched with acidified solution of cupric chloride (Stead's reagent)

51646°—21——6

3. CONTROL OF METALLURGICAL OPERATIONS AND PRODUCTS

A knowledge of the structure of an alloy, particularly a new one, will often aid materially in carrying out the mechanical working of the material satisfactorily. Fig. 55 shows the structure of a boron steel (Fig. 55 *a*—carbon, 0.16 per cent; boron, 0.49 per cent; nickel, 2.82 per cent; Fig. 55 *b*—carbon, 0.16 per cent; boron 0.39 per cent). When the attempt was made to roll these steels under the same conditions used with satisfactory results for steels of similar composition but containing no boron, the metal crumbled and cracked badly in the rolls. Indeed, some ingots were so brittle that they broke under their own weight when carried from the furnace to the rolls. By heating the ingots for a sufficiently long time until considerable coalescence of the eutectic occurred, and by reducing the temperature of the ingot somewhat, no unusual difficulties on working the metal were encountered. In a similar way oxide films and similar inclusions within a metal will often prevent such materials from being worked. In such cases a preliminary treatment of the molten metal must be made, usually a deoxidation treatment, for removing these undesirable features. Nickel is a good example; unless the metal is treated with magnesium or a similarly acting substance, it can not be satisfactorily rolled or worked hot in any way.

The conditions under which metals are cast have an important bearing upon the properties of the resulting castings. The examination of the microstructure often reveals features due to this cause which render the metal entirely unfit for use, although from a surface inspection the metal would be considered suitable for use. Fig. 3 shows a section of a large steel casting for a rudder frame which, although it had received the specified heat treatment and had been passed by the inspectors, broke during shipment, before it was ever put into use. The metal, which contained numerous inclusions and pores, though refined as to grain size by suitable heat treatment, still retained the initial dendritic or ingot structure because of the included impurities, and thus also the accompanying inferior properties. Temperature of casting has also an important effect on the properties of cast metal. If too cold, numerous "cold shuts," oxide films, and similar undesirable features are apt to occur on account of the sluggish flow of the metal. Fig. 56 illustrates such a condition in cast bronze. On the other hand, if too hot, a very coarsely

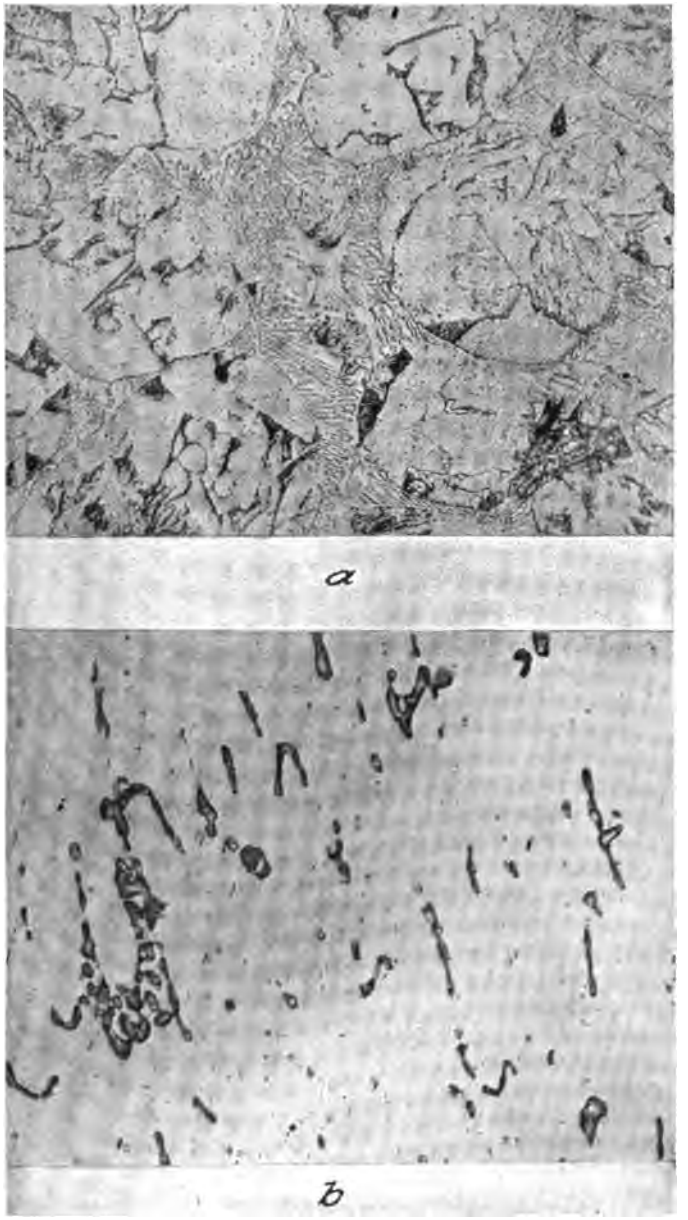


FIG. 55.—*Microstructure of low carbon steels to which additions of boron have been made.* × 500

(*a*) Section of an ingot of boron steel which broke in the rolls and could not be worked. The addition of the boron caused the formation of the eutectic shown; etching reagent, 2 per cent alcoholic solution of nitric acid. (*b*) Longitudinal section of a rolled plate of boron steel, showing the coalescence of the eutectic which has occurred. Etching reagent, hot alkaline solution of sodium picrate. This reagent colors the carbide a dark brown and sometimes nearly black

crystalline state results, the sand of the mold is rapidly eroded, and particles may be inclosed within the metal, gases absorbed by the metal during the overheating may be released, thus giving

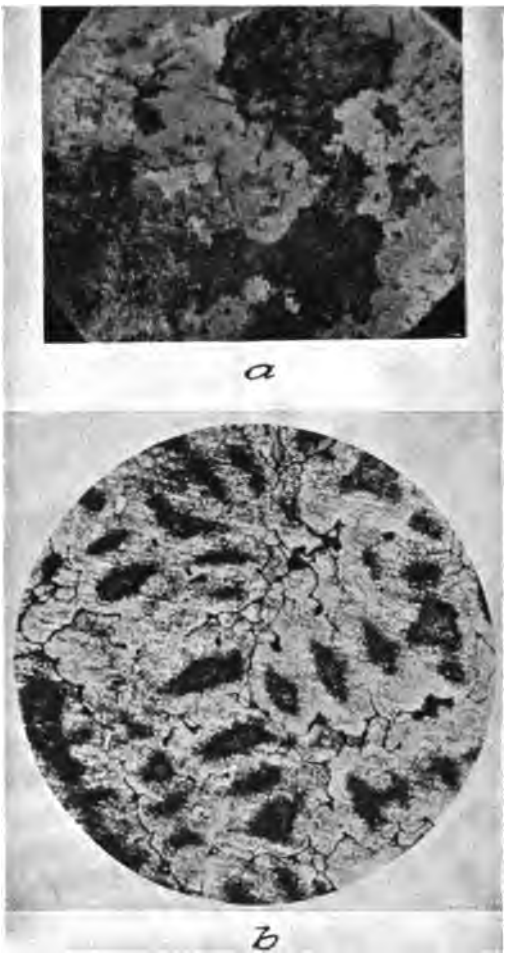


FIG. 56.—*Structure of inferior zinc bronze castings showing defects caused by improper conditions of casting*

Note the fine cracks within the individual crystals, *a*. The material is very much weakened by such a network as in *b*. (*a*) Macrostructure of cast bronze (approximate composition; copper, 88 per cent; tin, 10 per cent; zinc, 2 per cent), showing both intercrystalline and intracrystalline defects. Etching reagent, alcoholic solution of ferric chloride. × 5. (*b*) Defective cast bronze similar to *a;* numerous films, presumably oxide, and discontinuities exist between the branches of the dendritic crystals; etching reagent, ammonium hydroxide and hydrogen peroxide. × 100

rise to inferior castings, and undue segregation will readily occur in large castings during the very slow cooling.

The microscope is often valuable in determining the nature of certain metallurgical products masquerading under misleading

names. Thus, for example, the nature of wrought iron can be established with certainty by this means, "semisteel" can be shown to be only a particular grade of cast iron, having none of the characteristic properties of steel. An interesting example which may be cited is that of a specially prepared copper, advertised and sold as a deoxidizer for copper and other alloys. The examination of the material showed that the deoxidizer itself contained very appreciable amounts of cuprous oxide (Fig. 57). The "special treatment" given the material to render it a deoxidizer was not sufficient to prevent oxidation of the metal from occurring during the process of treatment. It appears plainly evident,

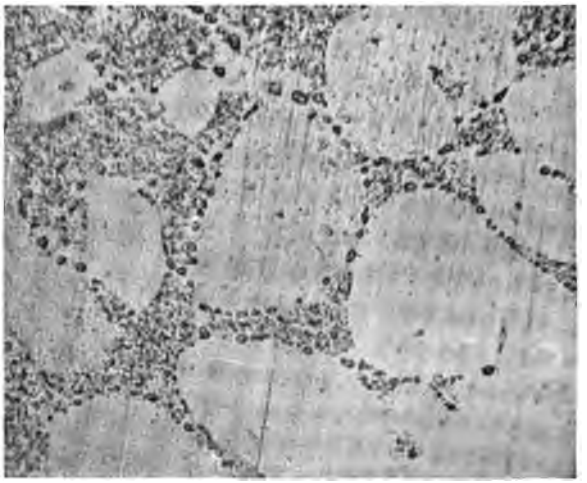


FIG. 57.—*Microstructure of a proprietary copper alloy recommended by the "inventor" for purposes of deoxidation of various alloys.* × 500

The metal as received from the makers contained numerous inclusions of cuprous oxide. Etching reagent, concentrated ammonium hydroxide.

then, that such a substance can have no appreciable deoxidizing effect upon an alloy to which it might be added. From time to time the Bureau of Standards has received for examination numerous specimens designated as "hardened copper," considered, according to the maker, as a rediscovery of "the lost art of tempering copper." A microscopic examination, supplemented at times by a simple chemical analysis, is usually sufficient to show the nature of the hardening process. A favorite method, probably unwittingly carried out, is to manipulate the melting process so that the metal becomes contaminated with oxide. This results in a much harder metal, but of course renders it unsuitable for the purposes for which copper is used.

Certain metallurgical processes are most readily and surely controlled by means of examinations of the structure of the product at various stages of the process. The manufacture of malleable iron offers a good example of this,[28] as does also its converse, the cementation process. The structural changes which occur during such processes as welding [29] and oxyacetylene cutting of metals affect the properties of the materials often to a very marked extent. Fig. 58 shows a block of steel which has been cut by the oxyacetylene flame. The metal has been affected to a very appreciable depth. An examination of this specimen after it had been annealed showed that the surface change in the metal, which at first sight may be mistaken for a carburized layer,

FIG. 58.—*Macrostructure of a steel block showing surface changes caused by cutting the steel by means of the oxyacetylene flame.* × 1

The surface was appreciably hardened for a considerable depth by the chilling action of the cool metal of the interior upon the hot metal of the surface after the flame was withdrawn. This sometimes causes cracks to form in the steel. It has also found special application for the surface hardening of steel. Etching reagent, aqueous solution of ammonium persulphate

was the result of the "quenching" action of the cold interior upon the hot metal at the surface after the removal of the flame. This special application of the action of a flame upon steel has been perfected and patented for the surface hardening of complex steel shapes, which would be distorted or would crack if hardened in the usual manner.

In the study of the mechanical working of metals it is often necessary to follow the material through the various stages through which it passes. In this connection the chemical unhomogeneity of metal, as has been indicated previously, serves a useful purpose; this is true in particular for phosphorus segregation, as this element diffuses extremely slowly so that the "flow lines" are clearly shown by its presence (Fig. 5). Other

[28] Enrique Tonceda, "Research work on malleable iron," Mechanical Engineering Journal, 41, p. 593; 1919.

[29] H. S. Rawdon, E. C. Groesbeck, and L. Jordan, Electric-Arc Welding of Steel—Properties of the Arc-Fused Metals, B. S. Tech. Papers, No. 179; 1920.

structural features often answer the purpose in other alloys; thus, as is shown in Fig. 59, certain discontinuities within a wrought round bar of Monel metal were clearly shown by the

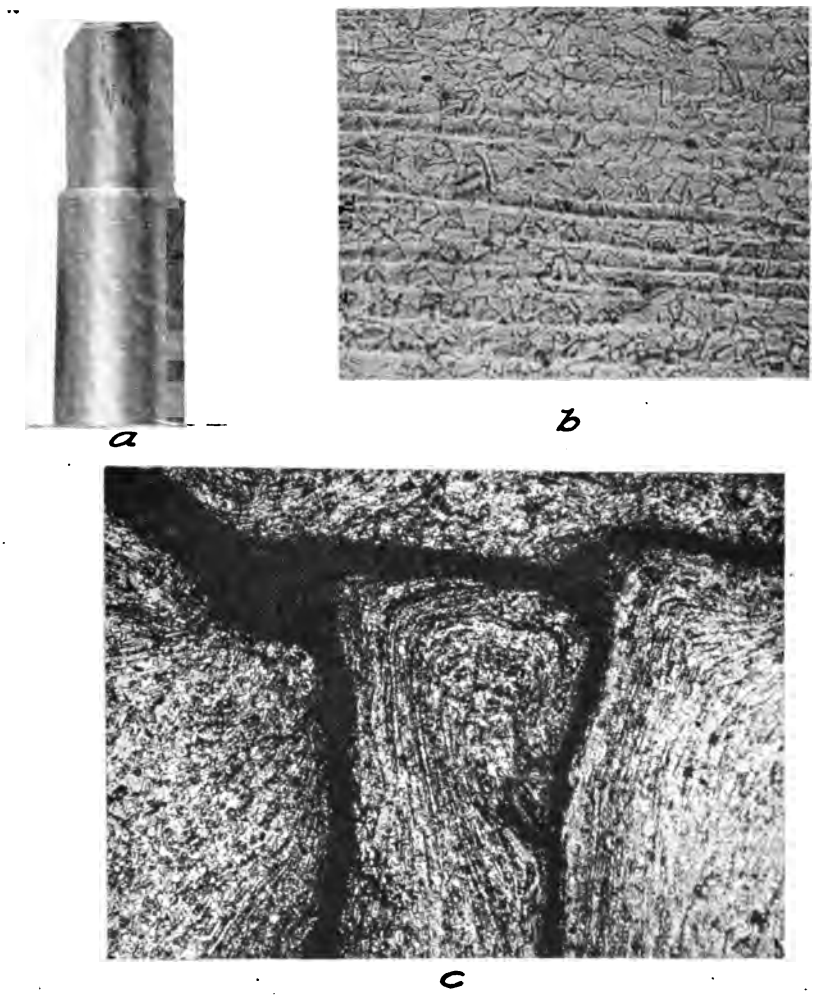


FIG. 59.—*Structure of monel metal showing interior defects originating before the metal was rolled*

(*a*) Monel metal rod showing an internal flaw. ×1. (*b*) Longitudinal section of sound monel metal showing "work lines." ×100. (*c*) Section through the defect in specimen *a*. The distortion of the "work lines" in the neighborhood of the defect proves that the defect existed in the metal previous to the rolling of it. ×50. Etching reagent, *b* and *c*, concentrated nitric acid

characteristic "work lines" to have had their origin while the metal was in a plastic state and not to have been produced by any treatment given the material subsequently by the user.

4. CONSTRUCTION OF CONSTITUTIONAL DIAGRAMS

In the construction of the constitutional or equilibrium diagram of any alloy system, microscopic examination of the various preparations forms an important part of the study. Although the data obtained by the thermal study form the basis of the work by furnishing the framework of the diagram, there are many features which must be checked by other means and some which can be determined by microscopic study only. The horizontal lines of a constitutional diagram are, in general, readily estab-

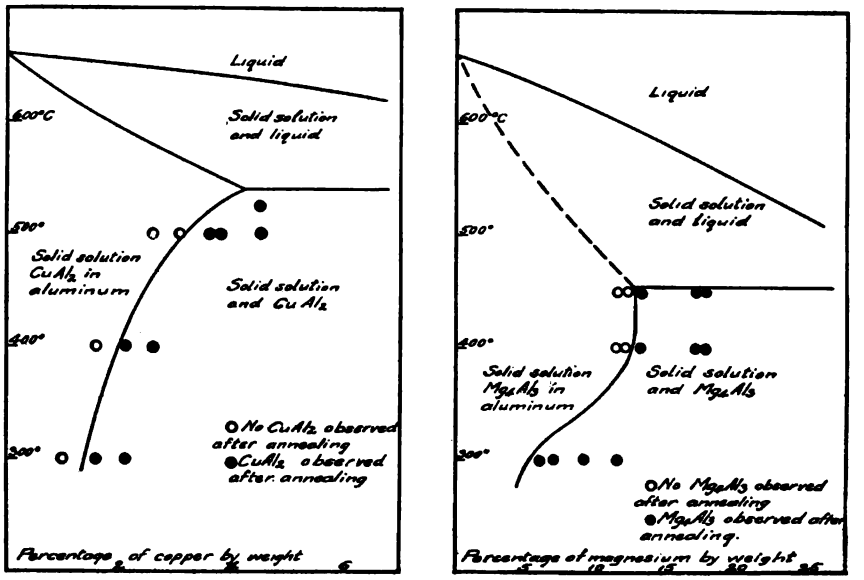


FIG. 60.—*Portion of the constitutional diagram of the copper-aluminum and of the magnesium-aluminum alloy system illustrating the use of microscopic examinations in the preparation of such diagrams*

lished by the method of thermal analysis; the vertical ones, those which mark the composition boundaries of structural "fields," depend almost entirely upon the microscopic study. An example of this use of the microscope is illustrated in Fig. 60, which shows how the limit of solubility of certain of the intermetallic compounds which occur in aluminum alloys was determined by the method of prolonged heating of specimens at certain temperatures followed by microscopic examination of the heated specimens. The matter of solubility of these compounds is of very considerable importance in connection with the subject of the hardening of aluminum alloys upon aging.[30] The microscopic method is also

[30] P. D. Merica, R. G. Waltenberg, and H Scott, The Heat Treatment of Duralumin, B. S. Sci. Papers, No. 347; 1919.

used extensively in verifying the conclusions tentatively arrived at as a result of the data obtained by thermal analysis or other means.

5. FAILURE OF METALS IN SERVICE

The investigation of the failure of metals which has occurred during service requires a wide and comprehensive knowledge of the properties and structure of metals, both sound and defective. The microscope has proved a very valuable aid in such studies and the structure often reveals evidence bearing upon the cause of failure which the ordinary methods of testing fail to detect. To discuss the relation of the microstructure to the failure of metals is impossible here; brief references only to a few specific cases will be used as examples.

Fig. 61 shows the appearance of a fracture which occurred in service in a 10-inch steel shafting. The fracture had the characteristic appearance of a "detail" or fatigue break which started in the angle of a keyway. The examination of the structure showed that it was almost a perfect one for such a failure; that is, for the particular composition of steel used (Fig. 61 *b*). Evidently the material had received no annealing treatment whatever for grain refinement after the forging of the shaft was completed. The large crystals with their prominent Widmanstättian structure are almost perfect, so far as failure to withstand repeated or vibratory stresses is concerned.

Fig. 62 shows the appearance of the fractured face of a Muntz metal bolthead which dropped off in service "of its own accord." Examination of the microstructure showed that the failure was the result of selective corrosion of the β-constituent, localized at the apex of the angle between the shank and head and accelerated by the service stress carried by the bolt. It can readily be shown [31] that corrosion of such alloys at the apex of a narrow groove (Fig. 63) is much more intense than elsewhere in the same material when the specimen is subjected to a tensile stress while surrounded by the corroding agent—for example, sea water. This behavior is to be attributed to the fact that the stress carried was not distributed equally in all cross sections, but was much higher at the bottom of the V groove than elsewhere. Under the combined action of corrosion, of the sea water and the service tensile stress carried by the bolt, the portion of the

[31] H. S. Rawdon, Typical Cases of the Deterioration of Muntz Metal by Selective Corrosion, B. S. Tech. Papers, No. 103. P. D. Merica, Failure of Brass: 2— Effect of Corrosion on the Ductility and Strength of Brass, B. S. Tech. Papers, No. 83.

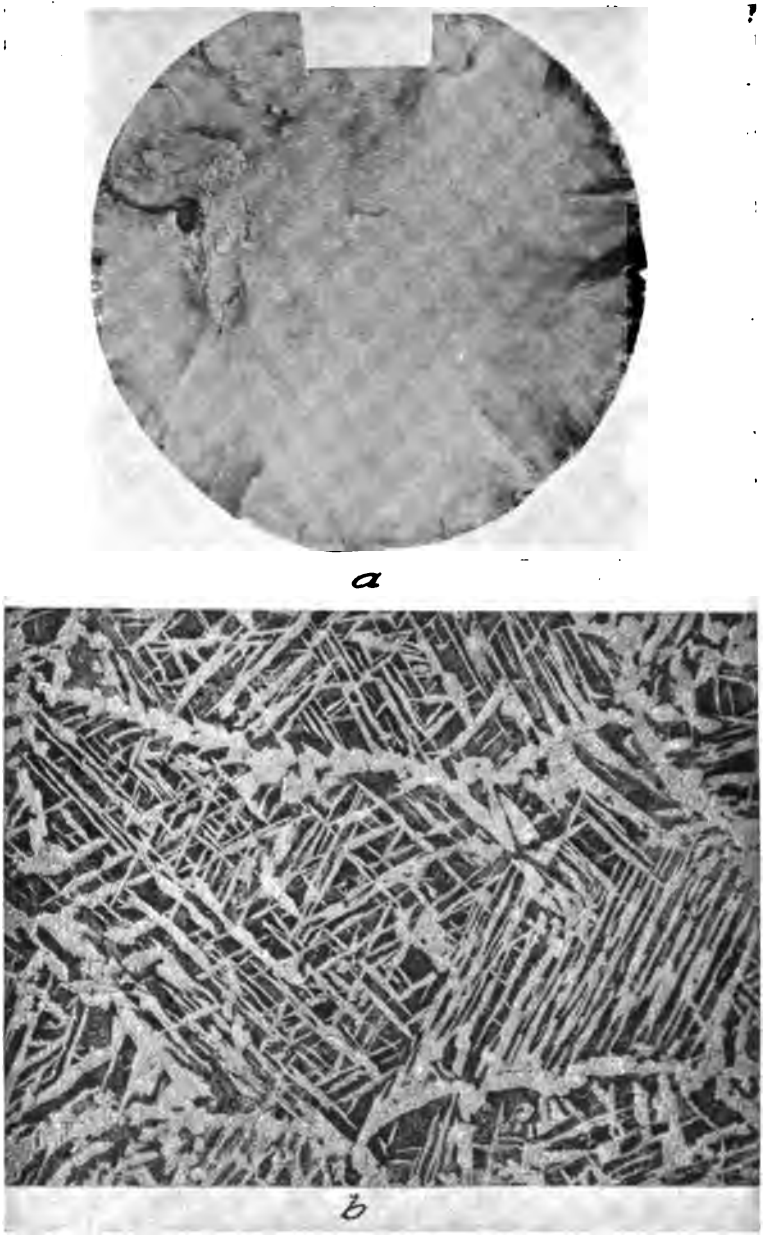
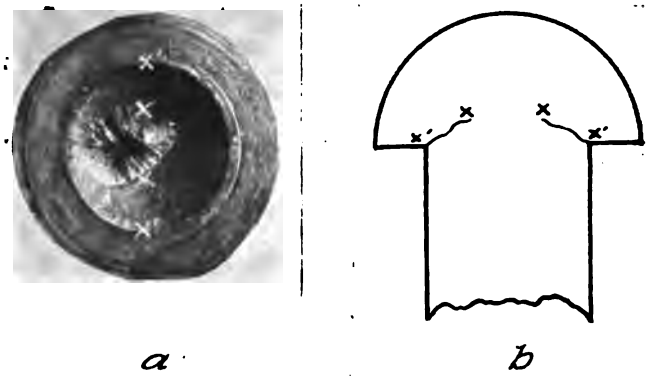
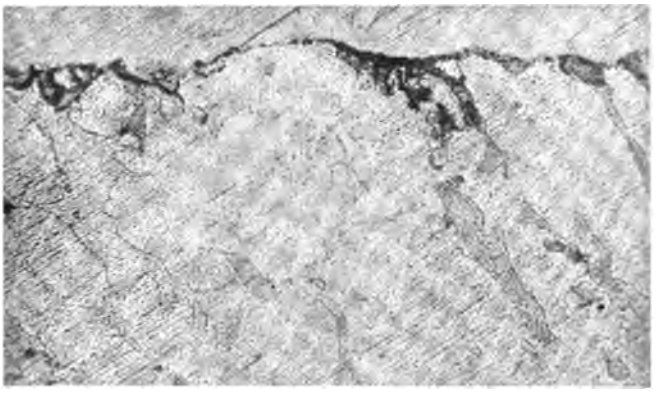


FIG. 61.—*Structure of a steel shafting which failed in service by fatigue*

Note the excessively large grain size, *b*. This was responsible for the service failure of the shafting. (*a*) Face of the fracture, which originated in a keyway. × ¼. (*b*) Microstructure of the metal of the interior. × 50. Evidently the forging received no treatment for grain refinement. Etching reagent, 2 per cent alcoholic solution of nitric acid





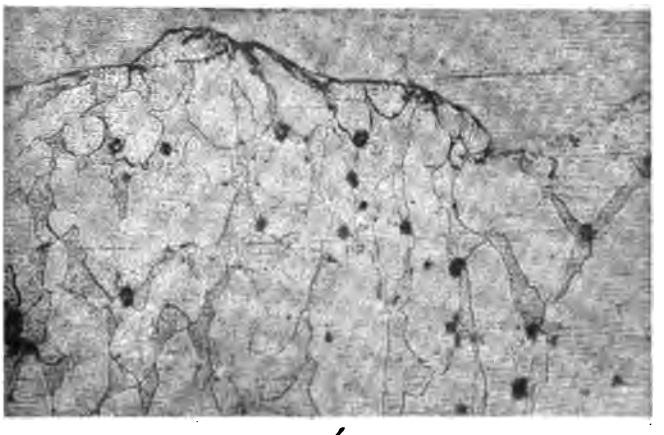


FIG. 62.—*Structure of a brass (Muntz metal) bolt which failed in service, evidently by being corroded while stressed in tension*

(*a*) Fractured face of the bolt head which dropped off of its own accord. × 1. (*b*) Longitudinal section of the bolt just before the head was detached. (*c*) Microstructure of the metal at the fracture in the portion x—x^1 of *a* and *b*. The β constituent has been dezincified by the corrosive action of the sea water to a considerable depth (black in micrograph) by corrosion. × 250. (*d*) Microstructure of the metal at the fracture in the central portion, x—x in *a* and *b*. No corrosion has occurred here; tensile stress alone caused the fracture of this part. × 250. Etching reagent, ammonium hydroxide

fracture x–x' was gradually produced; this has the appearance of a "detail" or fatigue break. When the cross-sectional area became small enough so as to break under the applied loading the central portion broke as a simple tensional break. The microstructure of the two portions confirms this; in the portion x–x' the β constituent at the extreme edge of the fracture showed evidence of deterioration by dezincification, while in the central portion the alloy was sound and unchanged up to the extreme edge of the fracture.

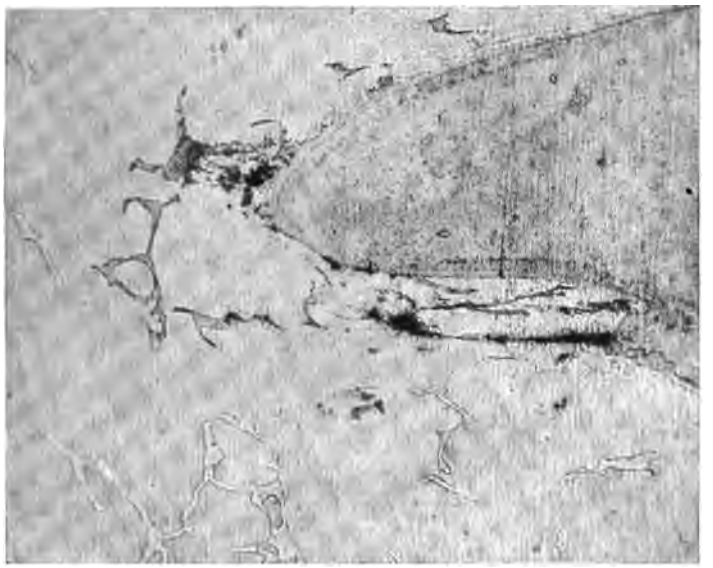


FIG. 63.—*Microstructure of corroded Muntz metal, illustrating the effect of stress in localizing the corrosive action of this alloy.* × *250*

A tensile specimen, ¼ inch diameter, encircled by a sharp narrow V-groove, was immersed in a 5 per cent solution of sodium chloride while under stress. The micrograph shows a section of the metal at the apex of the groove. Dezincification of the β constituent appears to have been accelerated by the relatively higher stress at the bottom of the groove. Etching reagent, ammonium hydroxide containing ammonium persulphate

Fig. 16 illustrates a failure which occurred in a railroad rail on account of the poor quality of the steel used. The rail showed evidence of a high degree of segregation, the portion adjacent to the split which occurred being of approximately 1.2 per cent carbon content, while the outer was much nearer the normal composition. Under the high pressure of the wheel loads the hard central streak was gradually shattered and the break extended until the split through the entire head of the rail resulted. There can be no doubt that the highly segregated nature of the metal was responsible for the failure in this case. It is not to be inferred,

however, that as a rule all segregated rails fail in service. The degree of segregation and the intensity and character of the service stresses decide.

6. SERVICE DETERIORATION OF ALLOYS

It sometimes happens that a metal or an alloy used for some specific purpose deteriorates, usually in a chemical way, under the peculiar conditions to which it is exposed, although for other purposes and for other conditions the material is suitable in every respect. An illustration of such deterioration is shown in Fig. 64, which represents an alloy essentially of aluminum and zinc (zinc, 85 per cent) used as a cover for a fuse box. The material was used in a tropical climate, and hence was exposed to conditions of high humidity and temperature, and the cover, originally flat, warped severely and bent out of shape. The surface showed characteristic "alligator" cracks. Fig. 64 *c* and *d* shows the appearance of two test specimens of a somewhat similar alloy intended for die castings after exposure to dry and to moist heat (100° C). Heat, in the absence of moisture, had no appreciable effect upon the material; the specimen retained its initial dimensions and shape. However, the sample exposed to the combined action of heat and moisture rapidly deteriorated by permanent expansion and distortion of the piece. An appreciable increase of hardness also accompanied this change. Microscopic examination showed that the eutectic was the portion attacked; presumably oxidation took place with accompanying increase of volume, the presence of moisture being necessary for this change to occur.

A somewhat similar change sometimes occurs in the filling used for fusible boiler plugs. The filling prescribed for such plugs is very high-grade tin. The presence of impurities in small amounts, particularly zinc, has been found[32] to stimulate the oxidation of the tin filling so that in time the plug filling becomes a hard infusible mass of oxide as shown in Fig. 65. In this case, as the above, the eutectic is the constituent which is most rapidly attacked and oxidized under the combined action of heat and moisture. A very considerable increase in volume accompanies the change in the tin filling of such plugs.

A somewhat different type of deterioration is illustrated in Fig. 66. The terminals in spark plugs are very often made of

[32] G. K. Burgess and P. D. Merica, An Investigation of Fusible Tin Boiler Plugs, B. S. Tech. Papers, No. 53.

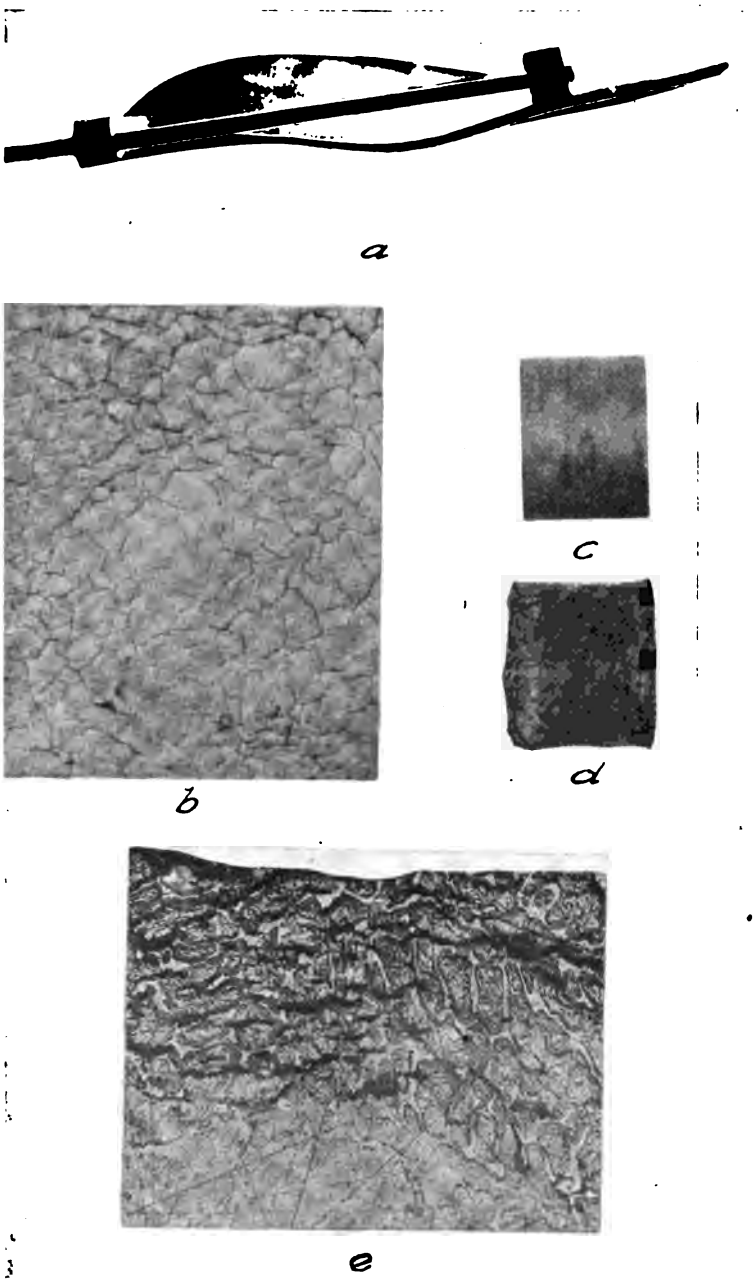


FIG. 64.—*Appearance of certain aluminum alloys of high zinc content after deterioration*

(*a*) Fuse box cover, approximate composition: Aluminum, 15 per cent; lead, 0.4 per cent; zinc, remainder; which was used in a tropical climate and warped in service. × ¼. (*b*) Surface of specimen, showing "alligator cracks." × 1. (*c*) Cylinder of an alloy, composition copper, 1.4 per cent; aluminum, 15.2 per cent, zinc, 83.4 per cent, exposed to "dry heat" (100° C) for 6 days. The dimensions of the specimen remained unchanged. × 1½. (*d*) Specimen similar to *c* exposed to "moist heat" (100° C) for 6 days. The specimen expanded and cracked. × 1½. (*e*) Cross section of specimen similar to *d*, showing the "expansion cracks" which formed in the metal near the surface by the action of heat and moisture; most of these occur in the eutectic; the specimen was unetched. × 100

nickel wire; these nickel terminals show more or less deterioration in all spark plugs on account of the high temperature and

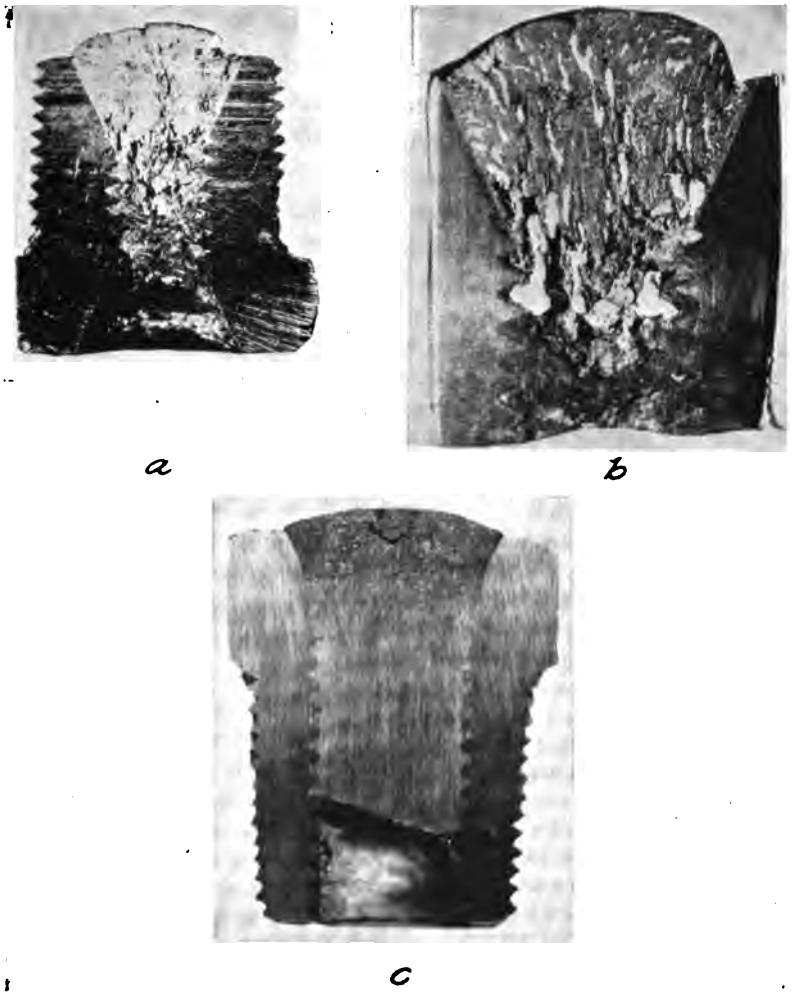


FIG. 65.—*Structure of safety boiler plugs which deteriorated in service*

Note the very considerable increase in volume of the filling of the plug which resulted from the deterioration. (*a*) Longitudinal section of a "safety" plug, to the deterioration of which was attributed the explosion of a marine boiler with considerable loss of life. The filling of tin was changed almost completely by service conditions into a hard refractory mass of tin oxide; a few globules of tin may still be seen in the interior. × 1. (*b*) Same specimen as *a*; the portion containing the filling has been polished so as to show the relative amounts of oxide and tin. The white areas are globules of tin; the remainder of the filling consisted of stannic oxide. × 2. (*c*) Longitudinal section of a plug used for four months, the tin filling of which has begun to deteriorate. The oxidation of the tin has occurred by the formation of a tree-like network permeating the tin. × 1

perhaps other conditions accompanying their use. This deterioration consists of an intercrystalline network which may in time

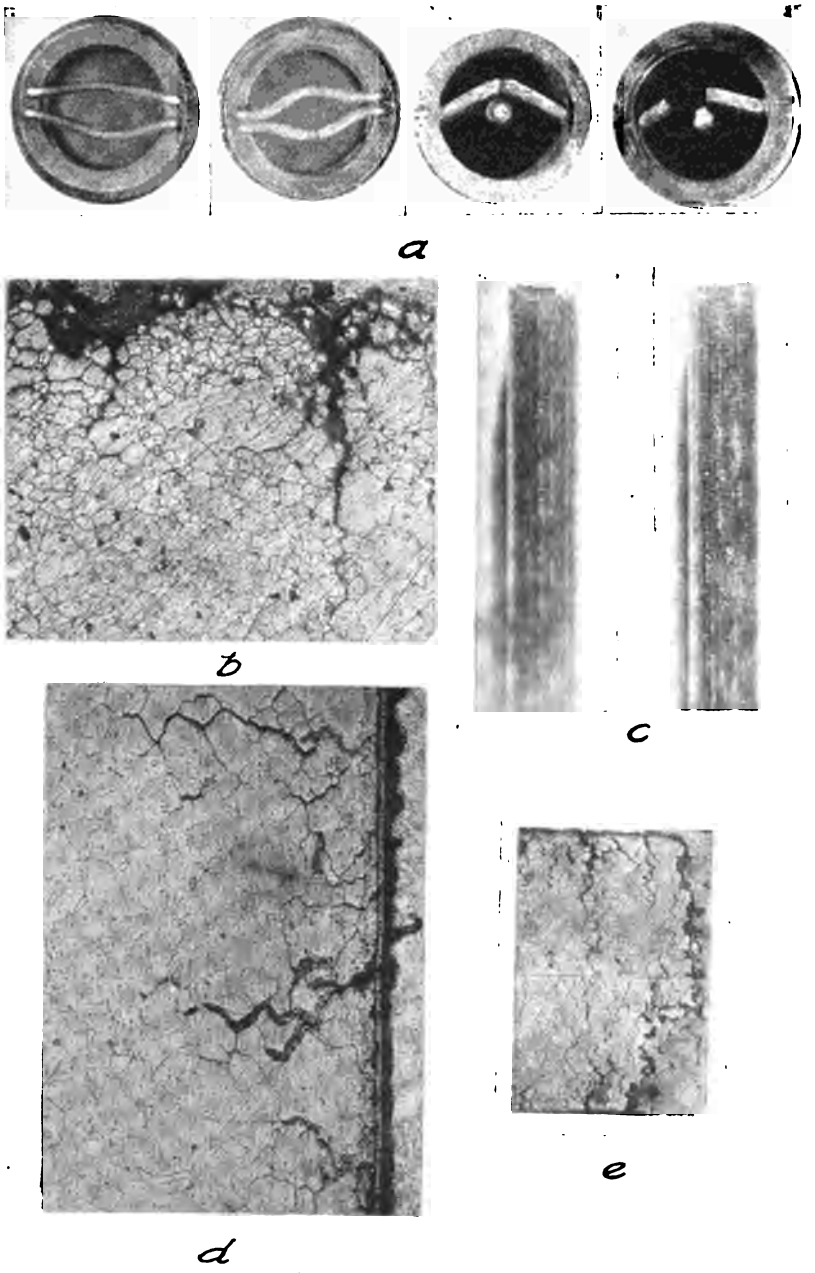


FIG. 66.—*The appearance of deteriorated nickel wire and tension specimens of the same tested at a high temperature*

Note the breaks in the wires of the spark plugs, *a*. These were the result of an intercrystalline attack of the nickel wire, as shown in *b* and *d*. (*a*) End view of four spark plugs the nickel electrodes of which have deteriorated in service. The wires have been severed transversely. × 1. The wires are anchored firmly at both ends so that considerable stress may be set up by differential expansion when the plug becomes heated. (*b*) Longitudinal section through one of the nickel wires of *a*, showing the network of intercrystalline fissures which formed in the metal during service, by which the severing of the electrode wires occurred. × 100. (*c*) Nickel wires broken by stressing in tension at approximately 900° C. The metal behaves as a brittle material under these conditions. × 5. (*d*) Longitudinal section of one of the wires of *c;* intercrystalline cracks and fissures identical in appearance with those of *b* have formed in the metal. ×100. (*e*) End of a nickel wire broken similarly to those of *c*. The fracture was entirely intercrystalline in its nature. × 25. Etching reagent, *b*, *d*, and *e*, concentrated nitric acid.

develop into visible intercrystalline fissures or cracks. A study [33] was made of various types of spark plugs, and it was found that in plugs of certain design the nickel terminals were subject to more or less tensional stress while hot, and in such cases the deterioration was very pronounced—very deeply penetrating cracks formed which soon severed the entire wire. It was shown by the microscopic examination of similar wires which had been subjected to the combined action of tensional stress and heat that the material deteriorated in a manner identical in appearance with that of the terminals of the spark plugs in service (Fig. 66 *c*, *d*, and *e*).

7. MISCELLANEOUS

A knowledge of the microstructure of metals and alloys is also useful in a great number of miscellaneous ways, of which the following are mentioned as interesting and typical examples.

(*a*) ELECTROLYTICALLY DEPOSITED METALS.—Fig. 67 shows the structure of copper which has been deposited electrolytically under different conditions of current density, and also the same materials after annealing. Copper deposited slowly forms relatively large regular crystals which change little, if any, upon subsequent annealing. On the other hand, copper deposited at higher current densities forms smaller and more irregularly shaped crystals, many of which are twinned. Upon annealing, such deposits behave exactly like copper which has been previously distorted by cold working.[34] The metal recrystallizes, grain growth follows, and the structure presents an entirely different appearance from that of the metal as deposited. It has been previously shown (Sec. IV, 2, *b*) that a change in the energy content of a metal by means of permanent distortion by cold working or similar means is a necessary condition for recrystallization of that metal upon annealing. It would appear, then, that metals deposited electrolytically may differ very materially in this same respect, according to the conditions under which they are laid down.

(*b*) BRINELL HARDNESS TESTS.—An interesting practical application of a knowledge of the microstructure of steel is illustrated in Fig. 68. This shows how advantage may be taken of the etching properties of the material of the steel ball used in the

[33] H. S. Rawdon and A. I. Krynitzky, A Study of the Deterioration of Nickel Spark-Plug Electrodes in Service, B. S. Tech. Papers, No. 143; 1920.

[34] H. S. Rawdon, "Note on the occurrence and significance of twinned crystals in electrolytic copper," Am. Inst. of Metals, **10**, p. 198; 1916.

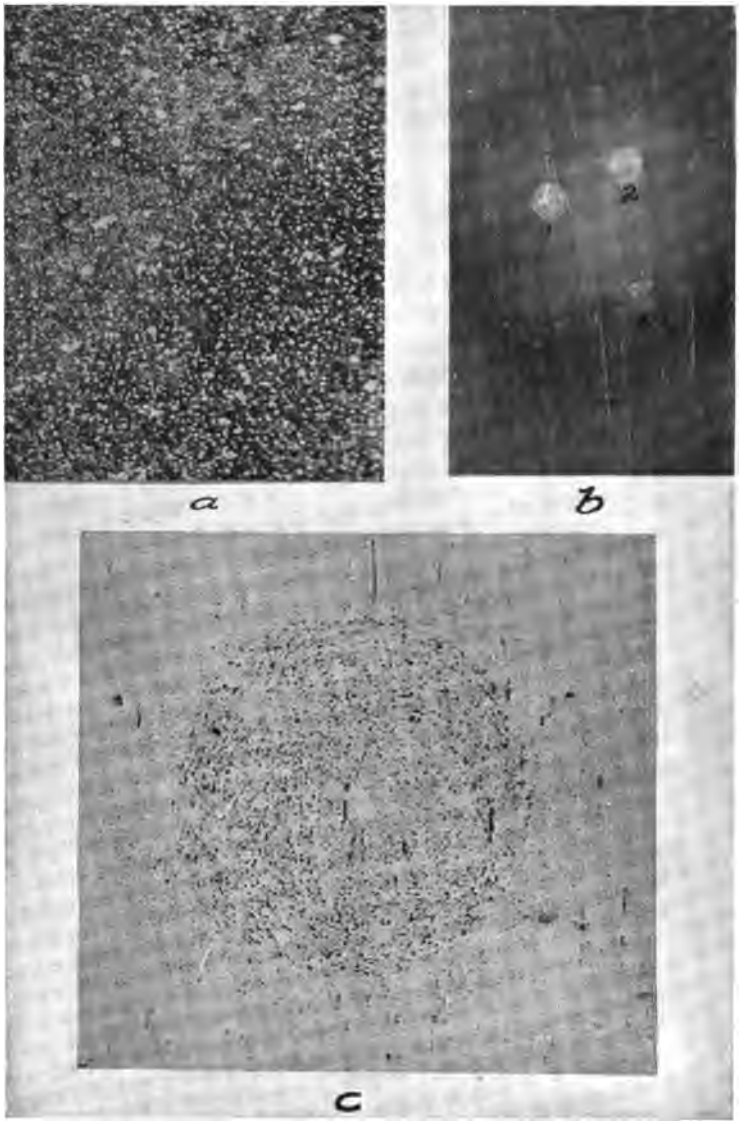


FIG. 67.—*Structure of electrolytic copper before and after annealing*

(*a*) Cross section of a sheet of electrolytic copper as deposited; current density, 0.41 amperes per square foot; temperature of solution, 38° C. The initial layer adjacent to the cathode face (right side) is finely crystalline. × 210. (*b*) Material similar to *a*, annealed 2 hours at approximately 600° C. The finely crystalline layer adjacent to the cathode face has recrystallized and shows twinned layers; the remainder, or coarsely crystalline portion, has remained unchanged. × 250. (*c*) Cross section of a sheet of electrolytic copper as deposited; current density, 0.73 amperes per square foot; temperature of solution, 25° C. Small, irregularly shaped crystals, many of which are twinned, are characteristic of this type of deposit. × 210. (*d*) Material similar to *c* after annealing as in *b*. × 210. The metal has entirely recrystallized and grain growth occurred in a manner identical with that of copper which has been annealed after being cold-worked. Etching reagent, ammonium hydroxide (1—1) followed by hydrogen peroxide. In each case the metal was deposited in the direction shown by the arrow

"The plate on page 99 belongs above the title for Fig. 67;
the plate on page 98 belongs above the title for Fig. 68

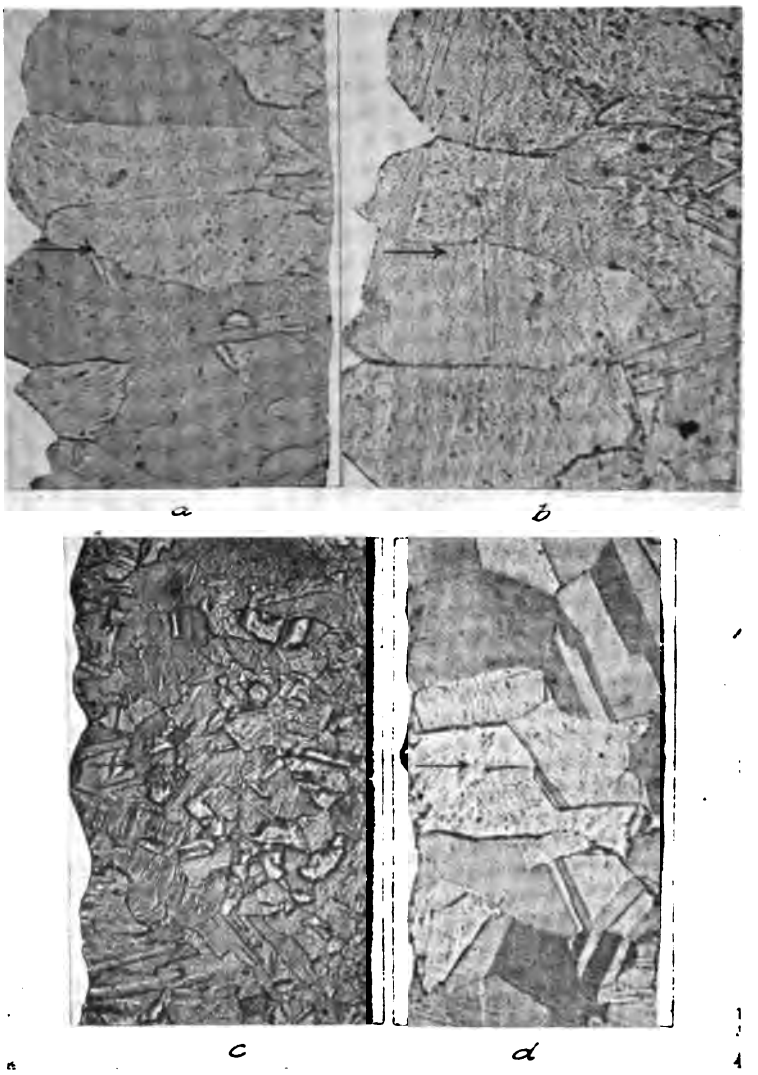


FIG. 68.—*Appearance of the etched surface of a ball used in Brinell hardness determinations and the indentations produced*

(*a*) Etched surface of hardened steel ball (chromium steel) used in Brinell hardness determination; etching reagent, 1 per cent alcoholic nitric acid. The white particles are the globules of carbide and are unattacked by moderate etching. × 500. (*b*) Brinell indentations produced on a polished specimen of file steel (carbon approximately 1.4 per cent), with a load of 1000 kg applied for 30 seconds on a 10 mm ball; 1 and 2 were obtained with an etched ball, 3 with a polished ball. The irregular spot at 3 is an ink mark for identification. × 3. (*c*) Indentation number 1 of *b*. × 50. The matt appearance of the indentations, 1 and 2, of *b* is the result of the great number of tiny pits produced by the carbide particles, which cover the face of the indentation. The indentation shows two distinct concentric zones, apparently caused by a difference in the pressure transmitted to the steel plate being tested

Brinell hardness test in order to obtain a higher degree of accuracy in the results when testing hard materials. The impression of the ball upon the surface of a hard metal, particularly if the latter is polished, is very indefinite, and the measuring of the diameter of the impression is a matter of considerable uncertainty. The ball used for the purpose consists practically always of a chromium steel of such a composition that in the hardened state it contains free carbide in the form of numerous rounded particles. By etching the ball slightly before use (2 minutes' immersion in 1 per cent alcoholic nitric acid) the "flowed metal" on the polished surface is removed, and the hard carbide particles are revealed. An impression made with such an etched ball upon a polished

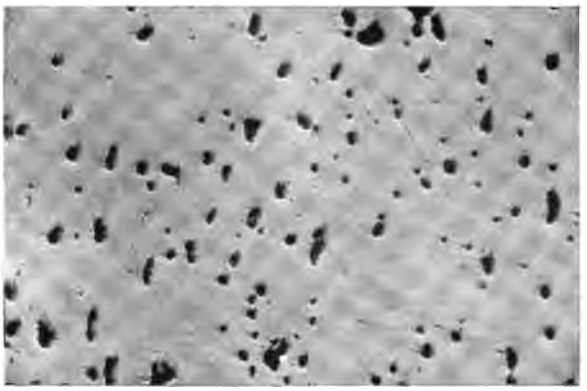


FIG. 69.—*Microstructure of leaded brass.* × 100

Each black spot represents a globule of lead added for the purpose of improving the machining properties of the alloy; the specimen was unetched

surface of a hardened steel is very much more conspicuous than one obtained with a polished one (Fig. 68 *b*). When the high pressure is applied, the carbide particles produce a multitude of tiny pits over the surface of the indentation of the ball, thus giving a "mat finish" to the indentation which aids very materially in defining its limits.

(*c*) WORKABILITY OF METALS.—The successful behavior of metals in automatic devices for turning out finished articles, for example, the manufacturing of screws in an automatic lathe, depends largely upon the ability of the material to produce turnings which are essentially brittle and break easily so that no clogging results. Such a material is readily obtained in the case of steel by the addition of sulphur to the metal and in brass by the addition of lead. Both of these additions, lead in brass and sulphide in the steel, exist as small isolated particles which break up

the continuity of the metal so that long twisted turnings do not result. The appearance of the structure of metal used for such purposes is shown in Figs. 18 and 69.

The structure of a malleable-iron casting, in the automatic machining of which considerable difficulty was experienced, is shown in Fig. 70. The malleableizing process was carried to such an extent that a relatively thick surface layer of ferrite was formed on the casting. This constituent (pure iron) is soft and has very inferior machining properties.

(*d*) SERVICE TEMPERATURE OF METALS.—A record of the temperature attained by some metals during service, for example, in bearings, is sometimes recorded in the metal itself. Fig. 71 shows the appearance of a bearing bronze which became overheated in service. The structure of the metal at the heated surface was found to be identical with that of the same bronze quenched from a temperature slightly above 500° C. At this temperature (approximately 500° C) the eutectoid transformation occurs in bronze containing approximately 10 per cent or more of tin. It is evident from the appearance of the overheated bearing bronze as compared with the initial structure and the same after quenching from a temperature above that of the eutectoid transformation that the surface metal was heated to a temperature at least above that of the eutectoid transformation and then suddenly chilled by the mass of cooler metal backing it. Similar cases are encountered in steel and other alloys which undergo a structural transformation upon heating.

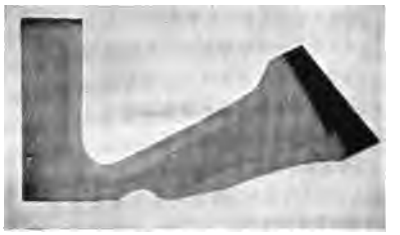


FIG. 70.—*Macrostructure of a malleable-iron casting with which difficulties were experienced in the automatic machining to size.* × 1

The metal at the surface (light-colored layer) was entirely decarburized in the "malleablizing" process and a thick layer of ferrite resulted. This constituent is soft and "gummy," and machines with difficulty. The specimen is unetched

(*e*) STRESS DISTRIBUTION IN MECHANICAL TEST SPECIMENS.—As previously stated (Sec. IV, 2, *b*), recrystallization of metals upon annealing necessitates a previous distortion of the crystals, usually by cold working. An interesting application of this fact to the study of the distribution of stress in specimens used for the various mechanical tests has been suggested by Chappel.[35] The specimen, which should be annealed first to remove any traces of

[35] C. Chappel, "Recrystallization of deformed iron," J. Iron and Steel Inst., 89, p. 460; 1914.

previous crystalline distortion, is tested and then annealed at a relatively low temperature, which in the case of steel must be below the transformation temperature. Recrystallization and

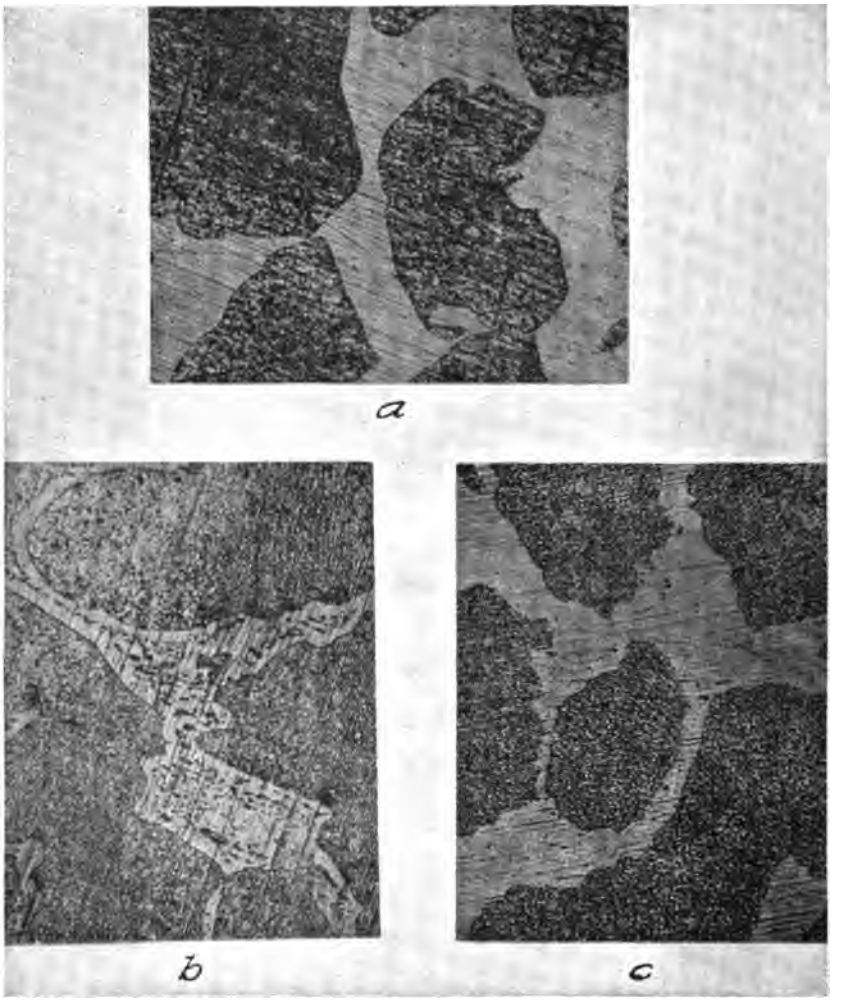


FIG. 71.—*Microstructure of a bronze used for a bearing which became overheated in service.* × 500

Note the light constituent which appears to be uniform in its structure, *a*. This appearance indicates that a temperature of at least 550° C was reached in the bearing. (*a*) Structure of the alloy adjacent to the heated surface of the bearing. (*b*) Structure of a specimen of the same alloy taken somewhat below the bearing surface; the alloy has its normal structure and consists of a eutectoid in a softer matrix. (*c*) Specimen similar to *b*, quenched in water after heating to approximately 550° C. The structure is identical with that of the alloy at the bearing surface. Etching reagent, concentrated ammonium hydroxide

grain growth will occur throughout the metal, the size of grain acquired differing, however, in different portions according to the stress to which the material was previously subjected. The

structure of the annealed specimen reveals then in an interesting qualitative way the distribution of the stress to which the specimen was subjected. The method gives most interesting results in the case of those tests in which a pronounced difference in the stress distribution occurs, such as the impact or shock tests.

VII. INFORMATION REGARDING TESTS

1. REPORTS

In general the Bureau will not in a formal report express an opinion as to the suitability of any metal or alloy for any specific purpose, this restriction to apply to proprietary alloys in particular. The results of the examination by which the properties and the structure of the material are determined will be given. Photomicrographs will be accompanied by statements as to the various constituents which are shown and the conditions under which the examination was made. In describing the microstructure of iron and steel the Bureau will conform, in general, to the Nomenclature of the Microscopic Substances and Structures of Iron and Steel, recommended by the sixth congress of the International Society for Testing Materials.

2. TESTS

For a proper and thorough understanding of any alloy and its properties a series of examinations is usually necessary—chemical, mechanical, thermal, and microscopic, as well as others for special purposes. In general, chemical analyses will be made by the Bureau for individuals, only in cases of dispute or when some question of very considerable scientific or technical importance is involved.

Most of the tests which the Bureau is called upon to make in connection with the physical metallurgy of metals are, with few exceptions, of a special nature, each one involving considerable investigation. The Bureau is equipped for studying in detail the methods of preparation of alloys and metals, the shaping of such metals by suitable mechanical working, and the properties of the resulting products, together with such related subjects as have a direct bearing upon these different processes. Such phases of the preparation of metals, as ore dressing, smelting processes, and the like, are not included. The Bureau of Standards' examination begins with the metal as such. The various metallurgical examinations which the Bureau is equipped for carrying out are listed below.